Catalysis of Copper Salts in the Liquidphase Oxidation of Hydrocarbons(Dissertation_全文)

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Preface

It has been well-known that liquid-phase oxidation of hydrocarnon is a radical chain reaction and consists of an initiation, propagation and termination steps.

$$RH \xrightarrow{k_1} R\cdot \quad (1) \text{ initiation step}$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \quad (2) \text{ propagation step}$$

$$RO_2\cdot + RH \xrightarrow{k_3} ROOH \quad (3)$$

$$2R\cdot \xrightarrow{k_4} R - R \quad (4) \text{ termination step}$$

$$R\cdot + RO_2\cdot \xrightarrow{k_5} ROOR \quad (5)$$

$$2RO_2\cdot \xrightarrow{k_6} ROOR + O_2 \quad (6)$$

Step(1) is an initiation step in which active radicals are formed. Step(2) and (3) are propagation steps in which R· or RO_2· acts as active species and constitutes radical chains. Step(4), (5) and (6) are termination steps in which R· or RO_2· rapidly disappears. When a concentration of dissolved oxygen is low, reaction(4) or (5) occurs, but in the presence of sufficiently high concentration of oxygen, reaction(6) predominates. Many metal salts, especially transition metals of the first series, are known as effective initiators; the process of metal salts to produce radicals is divided into three ways.

The first of these catalytic activities ever known is an activation of a molecular oxygen as proposed by Uri in

$$M^{+n} + O_2 \longrightarrow M^{+(n+1)}\cdots O_2^- \quad (7)$$

$$M^{+(n+1)}\cdots O_2^- + RH \longrightarrow M^{+n} + \cdot O_2H + R\cdot \quad (8)$$

the oxidation of methyl stearate catalyzed by cobalt salt.[1] Similar activations of oxygen were reported for copper phthalocyanine or copper polyphthalocyanine catalyst[2~4]

and discussed in detail for sulfonium or phosphonium catalysts.[5] However, these investigations seem to be paucy in direct evidence for the activation of oxygen.

More reliable deductions as for the activated oxygen have been obtained in the heterogeneous catalysis. It has been known that oxygen is rapidly adsorbed by metal ions such as zinc(II) oxide, titanium(IV) oxide or tin(IV) oxide; the forms of the activated oxygen have been taken as O_2^- or O^- by the use of ESR technique.[6 ~ 9] Similar

$$O_2(gas) \longrightarrow O_2^-(ads.) \longrightarrow O^-(ads.) \longrightarrow O^{2-}(lattice)$$

oxygen ion radicals have been proposed for vanadium(V) or chromium(V) catalysts.[9,10] Chemical reactivity of the adsorbed oxygen was also reported. Garner et al. observed the interaction between the adsorbed oxygen on copper(I) oxide with carbon monoxide or carbon dioxide and Ken et al. studied the reactivity of adsorbed oxygen toward carbon monoxide or nitrogen monoxide.[11] Many other researches have been carried out for the interaction of molecular oxygen with heterogeneous metal catalysts.[12~16]

The second is a direct abstraction of hydrogen atom from hydrocarbons by metal salts in higher valence state.

$$RH + M^{+(n+1)} \longrightarrow R\cdot + H^+ + M^{+n} \quad (9)$$

Bawn[17] reported that cobalt(III) salt or copper(II) salt abstracted hydrogen atom from benzaldehyde in glacial acetic acid and, later, Teramoto[18] reinvestigated this reaction in detail and confirmed that the abstraction of hydrogen atom by cobalt(III) ion functioned as a principal initiating step throughout the reaction. Brill reported that, in the oxidation of p-xylene in glacial acetic acid, cobalt(III) acetate abstracted hydrogen atom from p-xylene in the presence of methylethyl ketone.[19]

The third, the most important role of the metal

catalysts, is a radical formation by the decomposition of hydroperoxide (HPO). It has been reported that metal

$$\text{HPO} + \text{Metal salts} \longrightarrow \text{radical}$$

salts which have high activity in the decomposition of HPO are effective catalyst for the oxidation. For example, the order of various metal naphthenates to decompose p-methylbenzyl HPO is Co ≒ v ≒ Mn > Cu ≒ Cr > U ≒ Ni ≒ Fe > Zn ≒ Pb > Ba > Hg and that for the oxidation of p-xylene is Co ≒ Cr ≒ Ni > Mn > Fe > Zn > Pb ≒ Cu > Ba ≒ Hg. Transition metal salts such as cobalt, manganese or vanadium which have two or more stable valence states are considered to decompose HPO as shown below:

$$\text{ROOH} + M^{+(n+1)} \longrightarrow \text{ROO}\cdot + H^{+} + M^{+n} \qquad (10)$$

$$\text{ROOH} + M^{+n} \longrightarrow \text{RO}\cdot + OH^{-} + M^{+(n+1)} \qquad (11)$$

The ROO· radical is formed and metal ion is converted to the lower valence state simultaneously. (Eq. 10) Metal ion of the higher valence state is reproduced. (Eq. 11) The cycle of Eq. (10) and Eq. (11) decomposes HPO catalytically. This mechanism was proposed first by Haber et al.[20] Some other transition metals such as copper(II) or iron(III) were reported to be uneffective toward reaction (10) and the activities of metal ions toward Eqs. (10) and (11) are summarized as follows:

	V	Cr	Mn	Fe	Co	Ni	Cu
$\text{ROOH} \xrightarrow{Mn^{+n}} \text{RO}\cdot + M^{+(n+1)} + OH^{-}$	+*	+	+	+	+	+	+
$\text{ROOH} \xrightarrow{Mn^{+(n+1)}} \text{ROO}\cdot + H^{+} + M^{+n}$	±*	±*	+	-	+	-	-*

+ : positive, - : negative, * : not clearly confirmed

As may be seen in the table, copper salt seems not to

decompose HPO through reaction(10), but, instead, promote reaction (12) and it is considered that through the cycle of reaction(11) and (12) copper salt decomposes HPO catalytically.[22 ~ 25)]

$$R\cdot \xrightarrow{M^{+(n+1)}} R^{+} + M^{+n} \qquad (12)$$

Considerable discrepancies, however, have been observed in literatures for the mode of action of copper salts. On the other hand, some copper salts have much attention because of its specific activity for an activation of oxygen or an abstraction of hydrogen atom as mentioned above. Therefore it seems important to investigate the catalysis of copper salts in oxidation of hydrocarbon or in decomposition of HPO or interaction of copper salts with radicals produced during the oxidation.

The present thesis is composed of seven chapters.

Chapter 1 describes the decomposition of 1,2,3,4-tetrahydro-1-naphthyl HPO (secondary HPO) catalyzed by copper chlorides in pyridine or other basic solvents.[26)] In addition to the radical decomposition of the HPO catalyzed by copper(I) chloride, ionic dehydration catalyzed by copper(II) chloride - pyridine system is also studied.

Chapter 2 describes the decomposition of α,α'-dimethylbenzyl HPO (tertiary HPO) catalyzed by copper chlorides in pyridine.[27)] In this chapter, initiation of the decomposition by copper(II) species is discussed in detail.

In Chapter 3, the decomposition of benzyl HPO (primary HPO) catalyzed by copper chlorides in pyridine solvent is studied.[28)] The result is compared with those obtained in the decomposition of 1,2,3,4-tetrahydro-1-naphthyl and α,α'-dimethylbenzyl HPOs and the role of copper(II) salt - pyridine system in the elimination of α-hydrogen atom of primary or secondary HPO is discussed.

In Chapter 4, the interactions of copper(II) and cobalt(III) salts with HPO are studied on the basis of Molecular Orbital theory.[29] In addition to the consideration for the radical decomposition of HPO by these metal salts, the catalytic role of the copper(II) chloride - pyridine system in the ionic dehydration of primary and secondary HPOs is discussed.

Chapter 5 describes the autoxidation of cyclohexene catalyzed by copper(II) salts - alkali chlorides system in glacial acetic acid.[30] The effect of alkali chlorides on the catalytic activity of copper salts is discussed and compared with that of other alkali salts. Ligand transfer of copper(II) salt - chloride ion complex is also briefly described in the appendix.

In Chapter 6, the kinetics of the autoxidation of 1,2,3,4-tetrahydronaphthalene catalyzed by copper(II) salt - chloride ion complex is investigated. The effect of chloride ion to activate copper salt is also described.

In Chapter 7, the ESR spectra of various alkoxy and alkylperoxy radicals are studied.[32] Identification of the spectra of alkoxy and alkylperoxy radicals by their g-values is discussed. Also, hydrogen atom abstraction by these radicals is briefly described in the appendix.

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Chapter 1 Decomposition of 1,2,3,4-Tetrahydro-1-naphthyl Hydroperoxide Catalyzed by Copper chlorides in Basic Solvents

Introduction

Catalysis of copper salt in the decomposition of peresters, peroxides or hydroperoxides(HPO) has been described in a number of literatures[1~7], in which copper was considered to cycle continuously between its monovalent and divalent states by reacting with these peroxidic compounds and alkyl radical produced by the fragmentation of alkoxy radical as shown below:

$$ROOX + Cu^{+1} \longrightarrow RO\cdot + OX^{-} + Cu^{+2} \quad (1)$$

$$RO\cdot \longrightarrow R''=O + R'\cdot \quad (2)$$

$$R'\cdot + Cu^{+2} \longrightarrow R'^{+} + Cu^{+1} \quad (3)$$

(X : H, alkyl group or acyl group)

Most of these, however, dealt with the decomposition of only tertiary peroxidic compounds and, moreover, catalytic activity of copper salt in basic solvents has scarcely been investigated.

In our laboratory, it was found previously that the catalytic decomposition of cyclohexenyl HPO by copper salt was highly accelerated by the addition of various basic substances such as pyridine or hexamethylphosphoric triamide(HMPA).[8] Therefore, in this work, we have carried out the decomposition of 1,2,3,4-tetrahydro-1-naphthyl HPO (secondary HPO) catalyzed by copper chlorides in some basic solvents and the modes of the catalytic action of copper(II) and copper(I) chlorides were discussed separately in detail.

Experimental

Material 1,2,3,4-Tetrahydro-1-naphthyl HPO (THPO) was obtained by the autoxidation of 1,2,3,4-tetrahydronaphthalene according to the method reported by Hock.[9] Crude THPO was recrystallized twice from petroleum ether and stored under a nitrogen atmosphere to avoid moisture. 2-Propanol and pyridine were purified by the usual method. HMPA and other solvents (GR grade) were used without futher purification. Copper(II) chloride(anhydrous) used was the GR grade and copper(I) chloride was obtained by the reduction of copper(II) chloride dihydrate with sodium bisulfite.[10]

Apparatus and procedures In all cases, 40ml of solvent containing a known amount of the HPO was warmed to a desired temperature under a nitrogen atmosphere in a reaction vessel (capacity of 100ml) which was thermostatically controlled in an oil bath. In the case of the reaction catalyzed by copper(I) chloride, solvents were degassed to avoid an effect of dissolved oxygen. Under a magnetical stirring, a known amount of the solution containing a catalyst was added to the reaction vessel and the reaction was initiated. Reaction was followed by an iodometric titration of a remaining HPO as shown below: In a 300ml flask, 1g of sodium iodide and 50ml of glacial acetic acid were mixed under stirring. After 30 seconds, 3ml of a reaction mixture was added to it and the mixture was stored in a dark place under a nitrogen atmosphere for ten minutes. After dilution with 100ml of water, it was titrated with 0.1 N aqueous sodium thiosulfate.

Photo-decomposition of THPO was carried out under a nitrogen atmosphere by the use of a reactor equipped with a 200W high pressure mercury lamp of Taika Kogyo Ltd.

Visible spectra were observed by means of a Toshiba-Beckman U.V. spectrophotometer DBG. The apparatus

used in the ESR experiment was the JES-3BS-X type of Japan Electron Optics Laboratory. ESR spectra were measured at -196°C.

Analytical procedures Analysis of the reaction products(α-tetralol and α-tetralone) was carried out using a Hitachi gas chromatograph 063 equipped with a flame ionization detector. The column packing was PEG 1000 (2m) and the column temperature was maintained at 150°C. Water was analyzed by means of a Hitachi gas chromatograph 063 equipped with a thermal conductivity detector. The column packing was chromosob 101(80 ~ 100 mesh, 1m) and the column temperature was maintained at 80°C.

Result

Decomposition by copper(II) salts in basic solvents

Decomposition of THPO catalyzed by copper(II) chloride was carried out in some basic solvents. As can be seen from Fig. 1, decomposition of THPO catalyzed by copper(II) stearate does not proceed so much in chlorobenzene. However, copper(II) chloride shows a high activity in basic solvents; for example, more than 80% of THPO is decomposed after 60 minutes in HMPA. In acetonitrile which is not so basic as pyridine or HMPA, an induction period appears at the initial stage of the reaction. This phenomenon is the same as that reported by Kochi, who pointed out that copper(II) changed to copper(I) state during the induction period. The discussion concerning the induction period will be carried out in the next chapter. Other transition metals such as cobalt(II) chloride or nickel(II) chloride were found to be inactive in these basic solvents.

Hereinafter, the activity of copper salts solely in pyridine will be discussed.

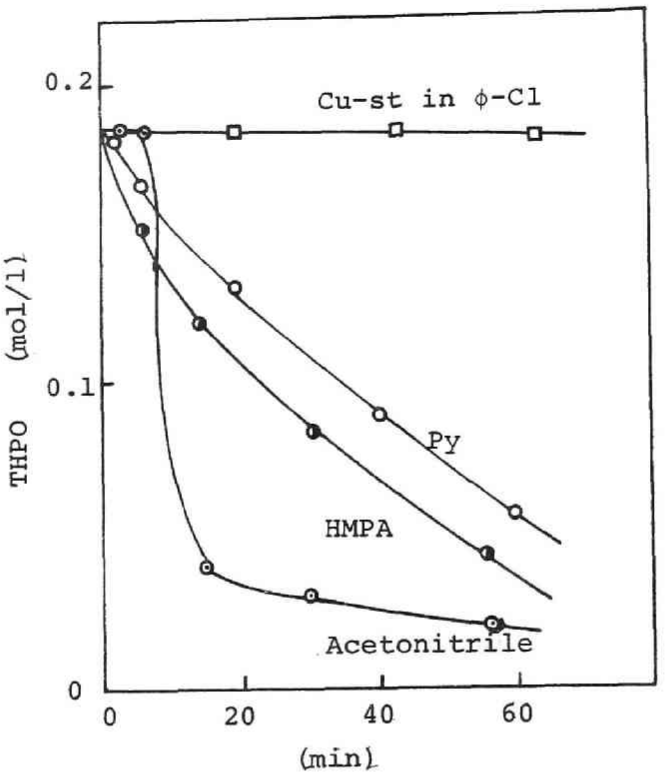


Fig 1 Decomposition of THPO in basic solvents

$[CuCl_2]$: 2.0×10^{-3} mol/l 40°C

Decomposition by copper(I) and copper(II) chlorides

Figs. 2 and 3 show the results of the decomposition of THPO catalyzed by copper(II) chloride in pyridine. It can be seen from the figure that the reaction proceeds without any induction period, which differs from the results reported by Kochi. The initial rate of the decomposition was found to be almost proportional to $[THPO]^1$ and $[Cu(II)]^1$ respectively and the rate constant was obtained as 8.13 l/mol.min.

Copper(I) chloride was found to be very active and approximately 90% of THPO was decomposed within a few minutes at 40°C. So the reactions were carried out at -15°C using a bath cooled with dry ice - methyl alcohol system. As shown in Fig. 4, decomposition proceeds

rapidly at the beginning of the reaction, but a retardation soon occurs and THPO is scarecely decomposed hereafter. It was found that the colour of the solution changed from yellow (before reaction) to green (after retardation), showing an absorption of visible spectrum at 730 nm due to copper(II) salt. The amount of THPO decomposed was found to be proportional to the concentration of copper(I) chloride added; 137 molecules of THPO were decomposed by one molecule of copper(I) chloride. When a co-catalyst system of copper(I) chloride - copper(II) chloride was used, it was found that the rate was independent of the concentration of copper(II) chloride , which, as well as the result of the visible spectrum, suggests that the deactivation occurs when all of copper(I) changes to copper(II)

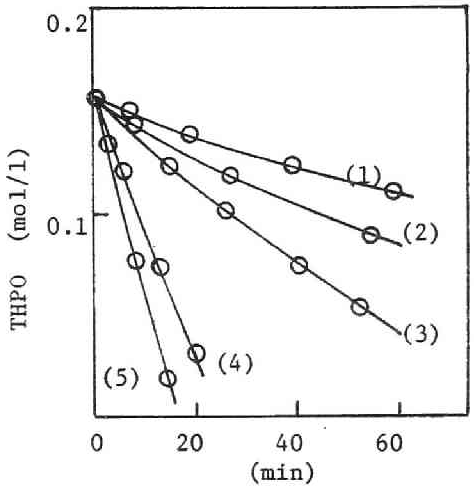


Fig. 2 Effect of $CuCl_2$ concentration
Solvent : Pyridine 40°C
$[CuCl_2]$ ($x10^3$ mol/l)
(1) 0.5 (2) 1.0 (3) 2.0 (4) 4.0
(5) 8.0

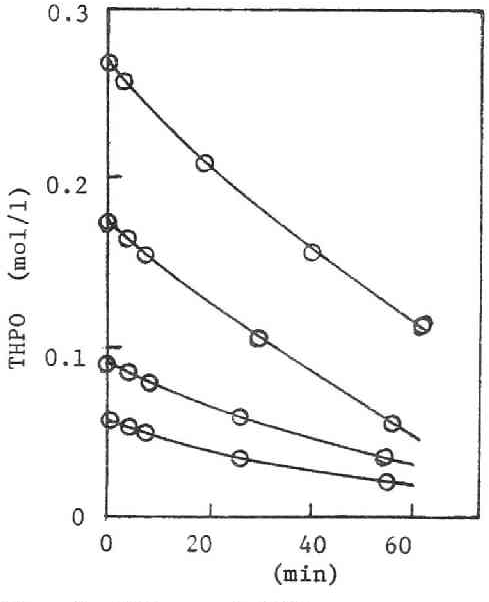


Fig. 3 Effect of THPO concentration
$[CuCl_2]$ $2.0x10^{-3}$ mol/l, Solvent: Pyridine 40°C

state. As it was expected that the reaction would again proceed by copper(II) salt when the temperature of the deactivated system was raised, the temperature dependence of the reaction was studied. As shown in Fig. 5, the catalyst recovers its activity with a rise in temperature but the rate is a little larger than that catalyzed by the same amount of copper(II) chloride. (see Fig. 2) As it seems that, in the latter case, the presence of dissolved oxygen may have been a cause for the decrease in the rate, the

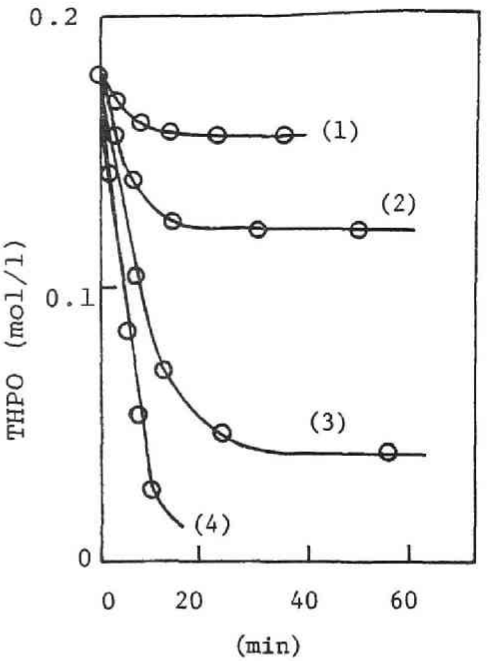


Fig. 4 Decomposition of THPO catalyzed by CuCl in pyridine at -15°C
[CuCl](x10^{3}mol/l) (1) 0.25 (2) 0.50 (3) 1.00 (4) 2.00

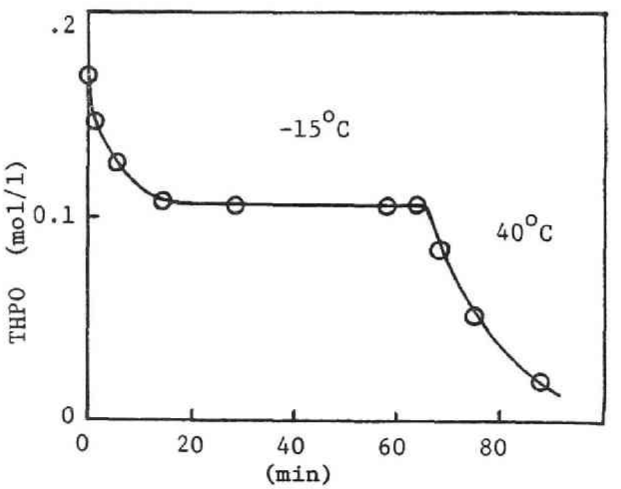


Fig. 5 Decomposition of THPO catalyzed by CuCl Effect of temperature
Solvent : Pyridine [CuCl] : 5.0x10^{-4}mol/l

effect of oxygen on the catalytic activity of copper(II) was investigated. It can be seen from Fig. 6 that the rate in the degassed pyridine is larger than that in the pyridine not degassed, which may imply that the initiation of the decomposition is caused by a trace amount of copper(I) species present as a mixture in copper(II) chloride. Therefore, prior to the reaction, the catalyst solution was refluxed for five hours under a oxygen atmosphere to oxidize traces of copper(I) to copper (II). As can be seen from Fig. 6, the rate of the decomposition is the same as that in pyridine not degassed and an induction period also cannot be observed, which shows that copper(II), as well as copper(I), has an ability to initiate the decomposition of THPO.

Temperature dependence of the reaction catalyzed by copper(II) chloride is shown in Fig. 7. We see that

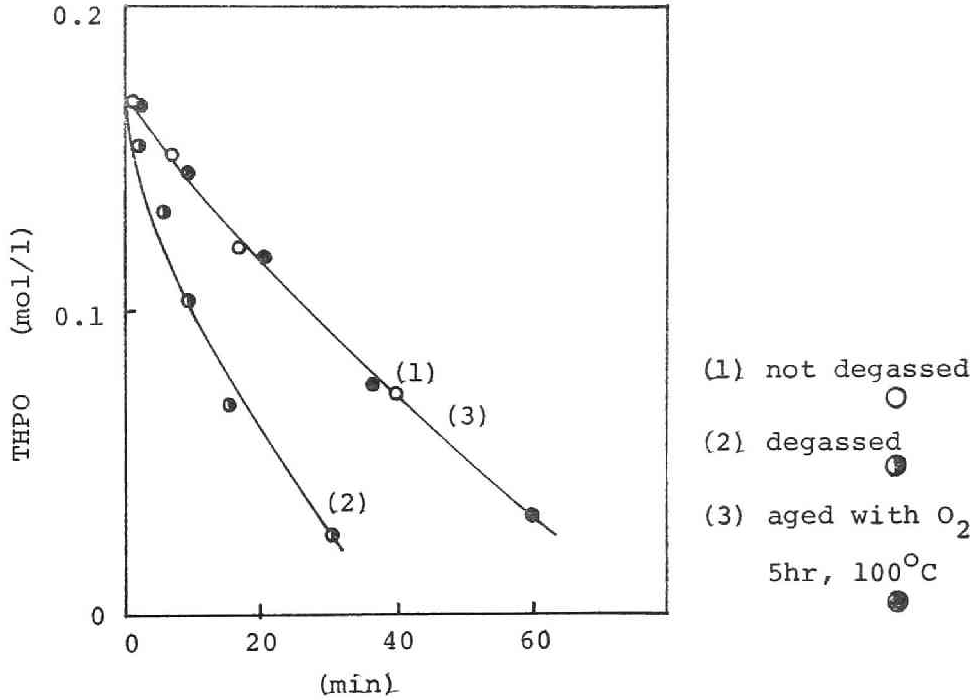


Fig. 6 Effect of O_2 40°C

Solvent : Pyridine $[CuCl_2]$:2.0×10^{-3} mol/l

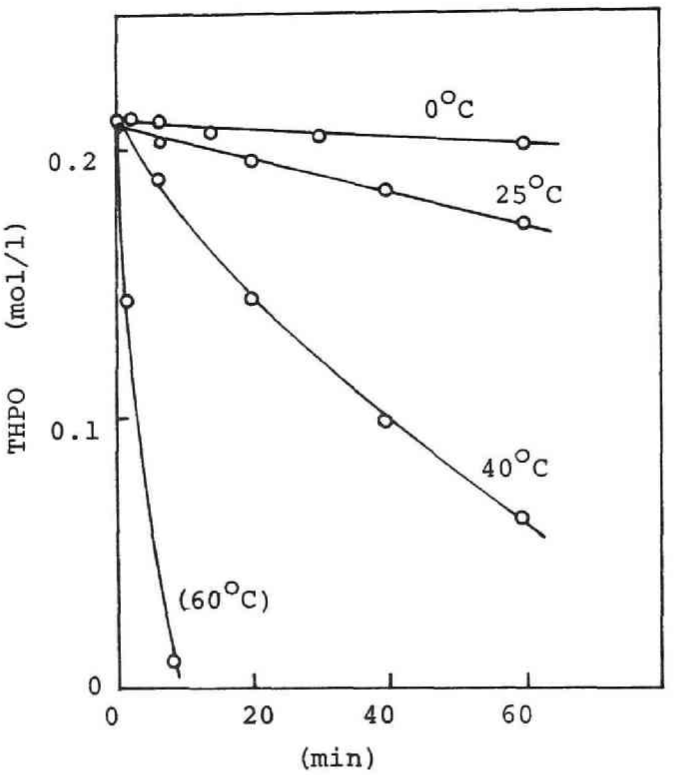


Fig 7 Effect of temperature

Solvent : Pyridine [$CuCl_2$] : 2.0x 10^{-3}mol/l

copper(II) chloride has only small activity at 0°C where the decomposition by copper(I) proceeds instantenously but that, in all cases, induction period cannot be observed. The activation energy of the reaction was obtained as 18.3 kcal/mol.

Effect of water Effect of water, one of the decomposition products, was studied and the result is shown in Fig. 8. As shown in the figure, the reaction catalyzed by copper(II) chloride is accelerated by the addition of water, but, in the case of copper(I) chloride, it retards the reaction. These results suggest that THPO is decomposed by different mechanisms in the case of copper(II) chloride and in the case of copper(I) chloride.

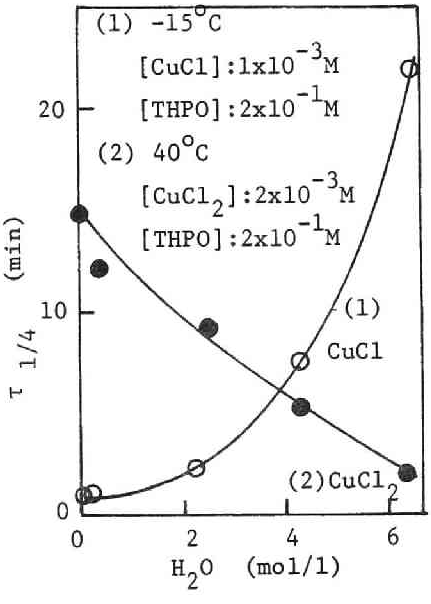


Fig. 8 Effect of water
Solvent : Pyridine

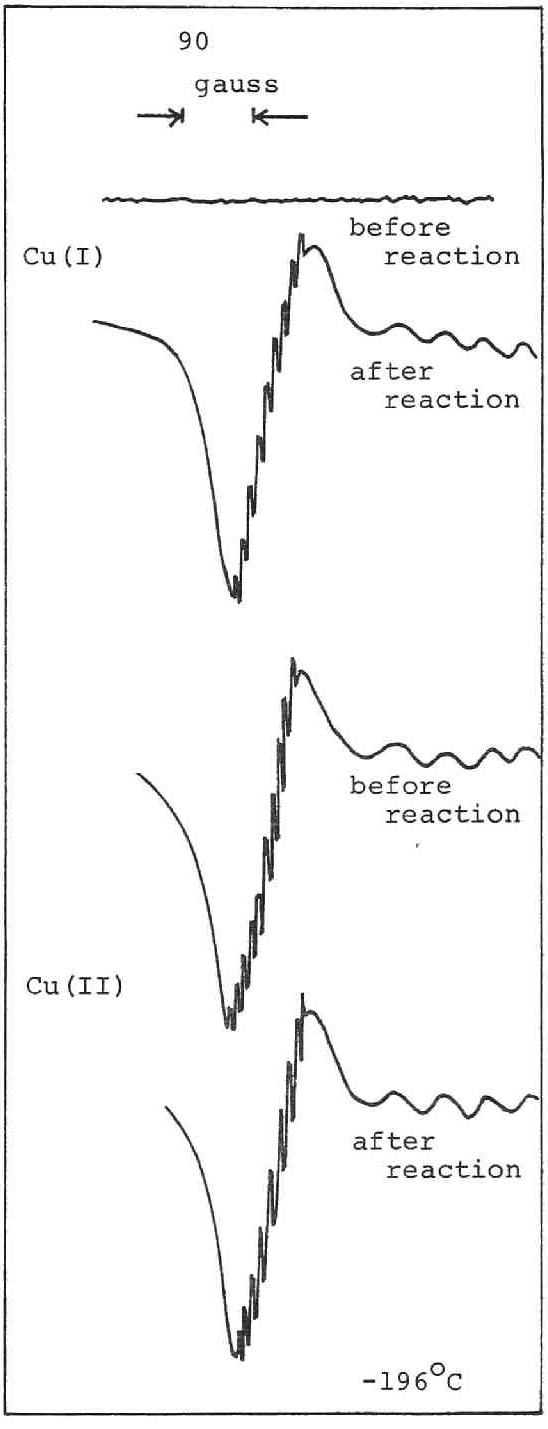


Fig. 9 ESR spectra of
copper-pyridine system

However, in both cases, water in such a trace amount as would be produced during the reaction has only a small effect. Mechanisms of the decomposition will be discussed in the later section.

ESR spectra In Fig. 9, ESR spectra of the catalyst system are shown. The procedure for the measurement of the spectra was as follows: A known amount of a catalyst in pyridine was added by a syringe into a sample tube containing THPO and, immediately, the tube was cooled with liquid nitrogen in a quartz dewar. We see that, in the case of copper(I) chloride, no signal can be observed before the reaction but that, immediately after the initiation of the reaction, a signal due to copper(II) species appears. The spectrum shows an anisotropic form in which the peak at highest magnetic field corresponds the resonance at $g_{//}$ and four peaks equally spacing corresponds the resonance at $g_{\perp}$, which shows that the complex has a square planar form. Moreover, seven to ten peaks are superimposed near the center of the spectra, which seems to result from the interaction between an unpaired electron of copper and a nuclear spin of nitrogen atom of pyridine coordinated to copper.[11] In the case of copper(II) chloride, there could be found no difference between the form of the spectrum or its intensity before and after the reaction.

Product distribution Product distribution in the catalytic decomposition of THPO by copper(II) chloride in some basic solvents is shown in Table 1. It can be seen that the yield of α-tetralone is increased as the increase of the basicity of solvent and that, in pyridine or HMPA, α-tetralone is selectively obtained. Table 2 shows the product distribution in pyridine in the catalytic and thermal decomposition. We see that, in all cases, α-tetralone and water are obtained almost quantitatively. Gaseous product could scarecely been

Table 1 Products of THPO decomposition in basic solvents

$[CuCl_2]$: 2.0×10^{-3} mol/l 40°C

Solvent	α-tetralone (%)	α-tetralol (%)
HMPA	100	0
Pyridine	100	0
DMFA	90.7	9.3
Acetonitrile	60.2	39.8

Table 2 Products of THPO decomposition in pyridine

Catalyst 2×10^{-3}M	THPO (M)	Temp. (°C)	α-Tetralone (M)	α-Tetralol (M)	H_2O (M)	Gas evolved
$CuCl_2$	0.172	40	0.167	0	0.165	0
CuCl	0.185	-15	0.184	0	0.167	0

Thermal decomposition at 120°C : α-Tetralone 97%
α-Tetralol 3%

detected in the catalytic decomposition, which suggests that peroxy radical(ROO·) is not a main intermediate during the reaction. Because, if peroxy radical is produced, considerable amount of oxygen must be evolved as shown by the following reaction.

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \qquad (4)$$

Discussion

As stated before, copper(II) and copper(I) chlorides both were found to be effective catalyst in the decomposition of THPO(secondary HPO) in pyridine, but the activity of copper(I) was much higher than that of copper(II). Moreover, the addition of water exerted different effect upon these two catalysts, that is,

water increased the activity of copper(II) but deactivated copper(I). From these results, it seems likely that, in pyridine, the mode of action of copper(II) chloride and that of copper(I) chloride differ from one another in decomposing THPO.

In the case of copper(I) chloride, a change from copper(I) to copper(II) could be observed at the beginning of the reaction by the use of ESR technique, which suggests that the initiation of the decomposition occurs by one-electron transfer as shown below:

$$ROOH + Cu^{+1} \longrightarrow RO\cdot + OH^- + Cu^{+2}$$

On the basis of the mechanism proposed by Kochi, the reaction scheme is described as follows:

$$ROOH + Cu^{+1} \xrightarrow{k_1} RO\cdot + Cu^{+2}\cdot OH^- \quad (5)$$

$$RO\cdot \xrightarrow{k_2} R'=O + H\cdot \quad (6)$$

$$Cu^{+2}\cdot OH^- + H\cdot \xrightarrow{k_3} H_2O + Cu^{+1} \quad (7)$$

$$Cu^{+2}\cdot OH^- \xrightarrow{k_4} Cu^{+2}\cdot Py + OH^- \quad (8)$$

Py : pyridine

Alkoxy radical and $Cu^{+2}\cdot OH$ are formed in Eq. 5, followed by the fragmentation of alkoxy radical to produce ketone and H· (Eq. 6). In Eq. 7, $Cu^{+2}\cdot OH^-$ oxidizes H· and Cu^{+1} is reproduced. We consider that the catalyst deactivates when $Cu^{+2}\cdot OH^-$ decomposes to an inactive $Cu^{+2}\cdot Py$ and OH^-. (Eq. 8) As stated earlier, 1 molecule of copper(I) decomposed 137 molecules of THPO and, from this, it can be assumed that the averaged ratio of the rate of the reactions (5), (7) and (8) is 137 : 136 : 1 respectively. The reaction scheme mentioned above leads to the rate expression for the decrease of Cu^{+1} as shown below:

$$d[Cu^{+1}]/dt = k_1[ROOH][Cu^{+1}] + k_3[Cu^{+2}\cdot OH^-][H\cdot]$$

$$= -1/137 k_1[ROOH][Cu^{+1}]$$

$$= -\alpha k_1[ROOH][Cu^{+1}] \qquad \alpha = 1/137 \qquad (9)$$

And the rate of the decomposition of THPO is

$$-d[ROOH]/dt = k_1[ROOH][Cu^{+1}] \qquad (10)$$

Elimination of dt from Eqs. (9) and (10) gives a differential equation, which is integrated as follows:

$$[Cu^{+1}] = [Cu^{+1}]_o - \alpha([ROOH]_o - [ROOH]) \qquad (11)$$

where $[ROOH]_o$ and $[Cu^{+1}]_o$ are the initial concentration of THPO and copper(I) chloride respectively. Substituting Eq.(11) into Eq.(10), Eq.(10) is solved.

$$[ROOH] = \frac{\beta\gamma\exp(k_1\beta t)}{\alpha\gamma\exp(k_1\beta t) - 1}$$

where

$$\beta = \alpha[ROOH]_o - [Cu^{+1}]_o \text{ and } \gamma = [ROOH]_o/[Cu^{+1}]_o$$

Calculated curves of the decomposition of THPO are obtained from Eq. (12) and compared with the experimental one. As can be seen from Fig. 10, there is considerable agreement between calculated and found values.

As described earlier, oxygen was found to be scarcely produced in the catalytic decomposition by copper(II), which shows that one-electron oxidation of the peroxidic bond of THPO by copper(II) does not play an important role during the reaction. Moreover, if it does occur,

$$ROOH + Cu^{+2} \not\longrightarrow ROO\cdot + H^+ + Cu^{+1}$$

active copper(I) is accumulated and the reaction must be

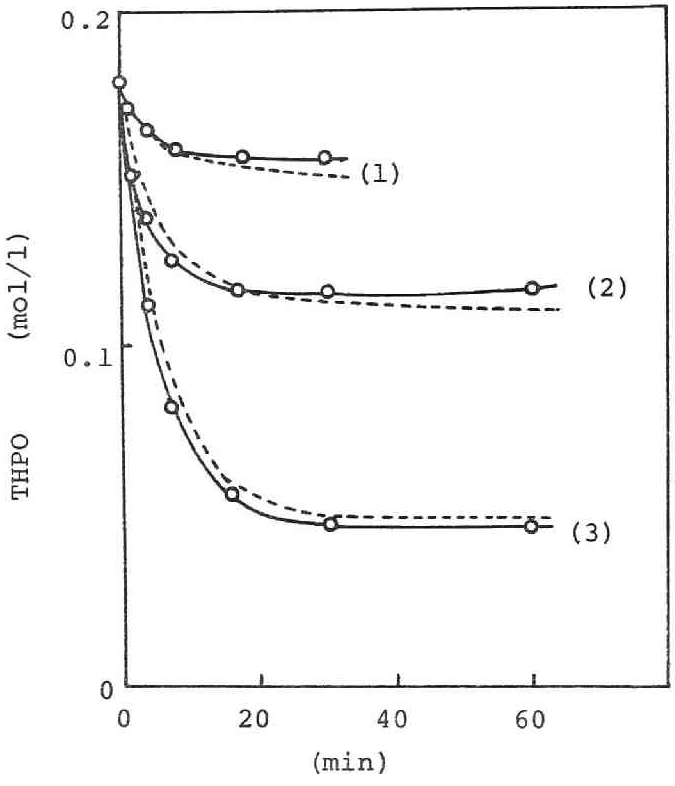


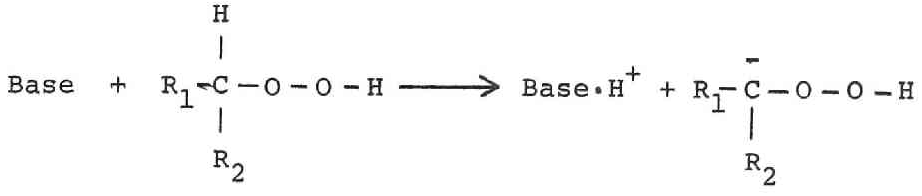
Fig. 10 Decomposition of THPO catalyzed by CuCl in pyridine at -15°C

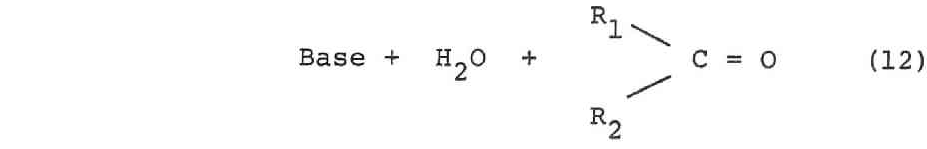
[CuCl] ($\times 10^{3}$ mol/l) (1) 0.25 (2) 0.50 (3) 1.00

——— : Exp. value, - - - - : Calcd. value

accelerated at the later stage. However, as can be seen from Fig. 2 or Fig. 3, no acceleration can be seen and, at the low catalyst concentration region, decomposition curves show an first order dependence on THPO concentration throughout the reaction. From these results, it seems that there is no change of the valence state of copper(II).

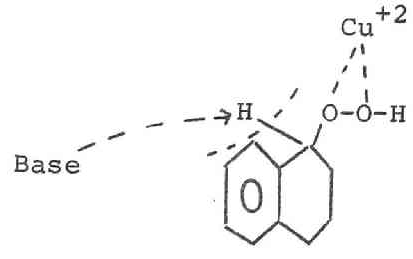
Ionic dehydration of secondary HPO by basic substances (Eq. 12) does not proceed at such a low temperature as 40°C,[12~14] but, from Fig. 1 and Table 1, it is clear that basic solvents play an important role in the decomposition of THPO catalyzed by copper(II). Therefore, we considered that copper(II) coordinated to the lone pair





(12)

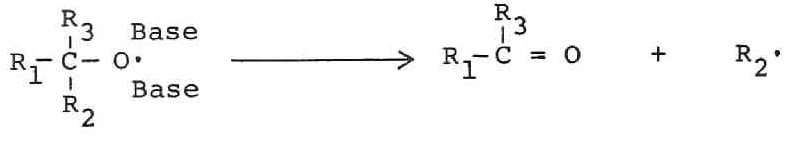
electron of the oxygen atom of THPO and weakened carbon-hydrogen bond of the α-position. In this way, the hydrogen will be easily abstracted as proton by basic solvents. The accelerating effect of water can be explained as producing OH^- ion, more basic than pyridine and capable of abstracting α-hydrogen, as shown below.



In the case of acetonitrile which is less basic than pyridine, an induction period appeared at the beginning of the reaction and α-tetralol as well as α-tetralone was found to be produced. (see Fig. 1 and Table 1) It seems that, in such a weak base, the reaction proceeds by a radical mechanism and that, as Kochi indicated, the change from copper(II) to copper(I) will occur during induction period.

Photo-decomposition of THPO in pyridine - 2-propanol mixed solvent As shown in Table 2, α-tetralone and water were exclusively obtained in the decomposition of THPO catalyzed by copper(II) chloride; the result can

be explained fairly well considering the ionic dehydration mechanism mentioned above. However, copper(I) chloride which seems to decompose THPO by a radical mechanism also promoted the formation of α-tetralone and water. This suggest that alkoxy radical formed in the decomposition of THPO by a radical mechanism is affected by basic solvent, pyridine. Walling [15] reported that in basic solvents, alkoxy radical was strongly solvated by these solvents and underwent fragmentation to form ketone and alkyl radical rather than abstraction of hydrogen atom from other substances. (see below)



To clarigy the effect of basic solvent on the behaviour of alkoxy radical, photo-decomposition of THPO was carried out in pyridine - 2-propanol mixed solvent and the result is shown in Fig. 11. We see that, as the ratio of pyridine to 2-propanol is increased, the yield of α-tetralone increases and that, in pure pyridine, it is selectively obtained, which is in good agreement with the result reported by Walling.

In the decomposition of THPO catalyzed by copper(I) chloride in pyridine - 2-propanol solvent, the yield of α-tetralone was also found to be increased as the increase of pyridine. However, in this case, α-tetralone was selectively produced in the solvent system of pyridine to 2-propanol ratio of 1 : 4 where fairly good amount of α-tetralol was formed in the photo-decomposition; which is not shown in figures. From the result, it seems that, in addition to the solvation effect of pyridine to alkoxy radical as Walling indicated, pyridine - copper system plays an important role for alkoxy radical undergoing fragmentation. This solvent effect will also be

discussed in Chapter 3.

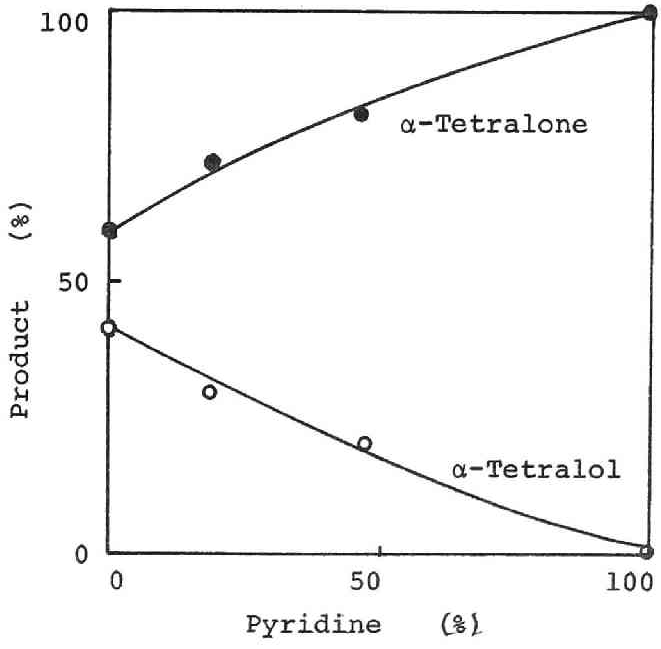


Fig. 11 Photo-decomposition of THPO in pyridine-2-propanol solvent 40°C

Summary

The experiment on the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (THPO) was carried out in pyridine or other basic solvents using copper chlorides as catalyst.

Copper(I) chloride was found to be more active than copper(II) salt. The addition of water, one of the products in the decomposition, increased the catalytic activity of copper(II) but, on the contrary, deactivated copper(I).

From these facts and the consideration based on the

observation of ESR spectra, it was concluded that copper(I) decomposed THPO by a radical mechanism and copper(II) by an ionic one, namely, ionic dehydration.

The products consisted of fair amount of α-tetralone and water in pyridine but considerable amount of α-tetralol was obtained in acetonitrile, which showed that the product distribution varied with the change of basicity of solvents. In connection with this, the experiment on the photo-decomposition of THPO was carried out in pyridine - 2-propanol mixed solvent and the behaviour of the alkoxy radical, α-tetraloxy radical, in basic solvents was discussed.

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Chapter 2 Decomposition of α,α'-Dimethylbenzyl Hydroperoxide Catalyzed by Copper Chlorides in Pyridine

Introduction

Detailed studies have been carried out by Kochi et al. concerning the catalytic activity of copper salts in the decomposition of various peroxides, peresters or hydroperoxides in non-aqueous solvents.[1~5] In their works, it was reported that the decomposition was initiated by the one-electron reduction of the peroxidic bond by copper(I) to form copper(II) species and alkoxy radical which yielded alkyl radical on fragmentation (Eqs. 1 and 2)

$$ROOH + Cu^{+1} \longrightarrow RO\cdot + OH^{-} + Cu^{+2} \quad (1)$$

$$RO\cdot \longrightarrow R''=O + R'\cdot \quad (2)$$

Copper(I) was considered to be reproduced by the subsequent copper(II) oxidation of the alkyl free radical (Eq. 3).

$$R'\cdot + Cu^{+2} \longrightarrow R'^{+} + Cu^{+1} \quad (3)$$

Copper(II), though effective in Eq.(3), was considered not to promote the direct oxidative decomposition of peroxide (Eq. 4) and, in the catalytic decomposition of peroxides by copper(II), an induction period appeared during which the change from copper(II) to copper(I) occured.

$$ROOH + Cu^{+2} \longrightarrow ROO\cdot + H^{+} + Cu^{+1} \quad (4)$$

However, there still remain some questions to the theory of Kochi concerning the induction period and the mode of the action of copper(II) salt.[6]

Previously, we have carried out the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (THPO) catalyzed by copper chlorides in basic solvents and suggested that copper(II)-basic solvent system promoted the elimination of α-hydrogen of THPO in an ionic mechanism.

In this work, decomposition of α,α'-dimethylbenzyl hydroperoxide (CHPO), which has no α-hydrogen atom, catalyzed by copper chlorides was carried out in pyridine and considerable attention has been focused on the catalytic activity of copper(II) salt.

Experimental

Material Commercial CHPO was washed with 1% aqueous sodium hydroxide to remove a trace amount of phenol which was a contaminant in CHPO. Adding 25% aqueous sodium hydroxide to this crude CHPO, sodium salt of CHPO was obtained. Then it was washed three times with cold ethyl ether and dispersed in water followed by bubbling CO_2 gas to liberate CHPO. CHPO was then extracted with ethyl ether and, after removal of ethyl ether, it was distilled twice under reduced pressure. CHPO purified in this method contained 98.6% of active oxygen. Copper(I) chloride was obtained by the reduction of anhydrous copper(II) chloride.[7] Commercial pyridine and acetonitrile were purified by the usual method. Other reagents (GR grade) were used without further purification.

Apparatus and procedures Apparatus used in the decomposition of CHPO and the procedures were the same as described in the previous chapter.

Analytical procedures The reaction products were analyzed using a Hitachi gas chromatograph 063 equipped with a flame ionization detector by the use of authentic samples and the yields were determined using

appropriate internal standards previously calibrated against the authentic samples. The conditions for the operation of the gas chromatograph were as follows:

Analysis of α-cumyl alcohol and acetophenone;

Column : PEG 1000 3mm$^{\Phi}$ xl m, Column temperature : 140°C, Carrier gas : N_2

Analysis of α,α'-dipyridyl;

Column : Silicone SE - 30 3mm$^{\Phi}$ xl m, Column temterature : 160°C, Carrier gas : N_2

Visible spectra of the reaction solution were observed by means of a Toshiba-Beckman U.V. spectrophotometer DBG. The apparatus used in the ESR experiment was the JES-3BS-X type of Japan Electron Optics Laboratory. Associated state of CHPO in the reaction mixture was discussed using a Hitachi Infrared Spectrophotometer 215.

Result and Discussion

Decomposition by copper(I) chloride Decomposition of CHPO catalyzed by copper(I) chloride was carried out in pyridine at 0°C. It can be seen from Fig. 1 that the reaction proceeds without any induction period, which shows that copper(I) has a high activity to decompose CHPO as in the case of THPO. (see Chapter 1) However, the catalyst soon lost its activity and it was found that one molecule of copper could decompose only ten to fifteen molecules of CHPO. The colour of the solution was yellow at the beginning of the reaction but changed to green due to copper(II) species formed during the reaction and finally to brown, liberating the catalyst as a brown precipitate. Fig. 2 shows the rate dependence on CHPO concentration. From Figs 1 and 2, the rate was found to be proportional to $[\text{Copper(I)}]^{0.95}$ and $[\text{CHPO}]^{1.0}$. Catalytic activity of copper(I) chloride was also investigated in acetonitrile which is less basic than pyridine and the results are shown in Fig. 3 and Fig. 4. From Fig. 1 ~ Fig. 4, it will

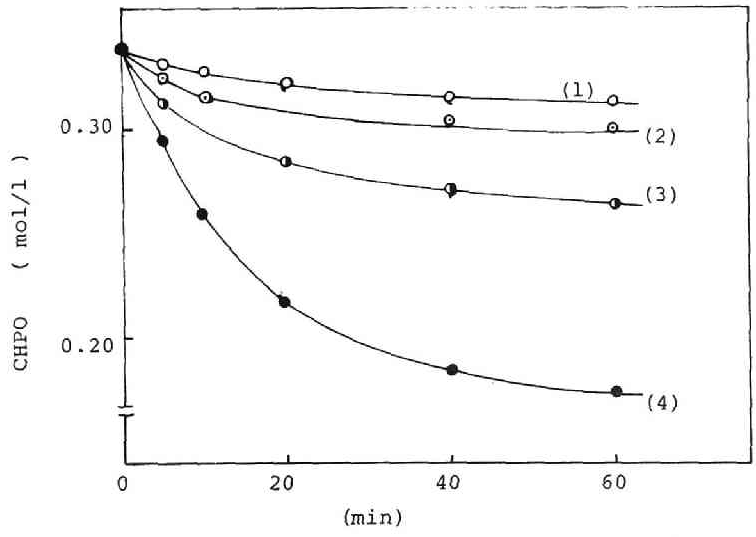


Fig. 1 Decomposition of CHPO catalyzed by CuCl in pyridine at 0°C

[CuCl](mol/l) — (1) 2.0×10^{-3} (2) 4.0×10^{-3}
(3) 8.0×10^{-3} (4) 1.6×10^{-2}

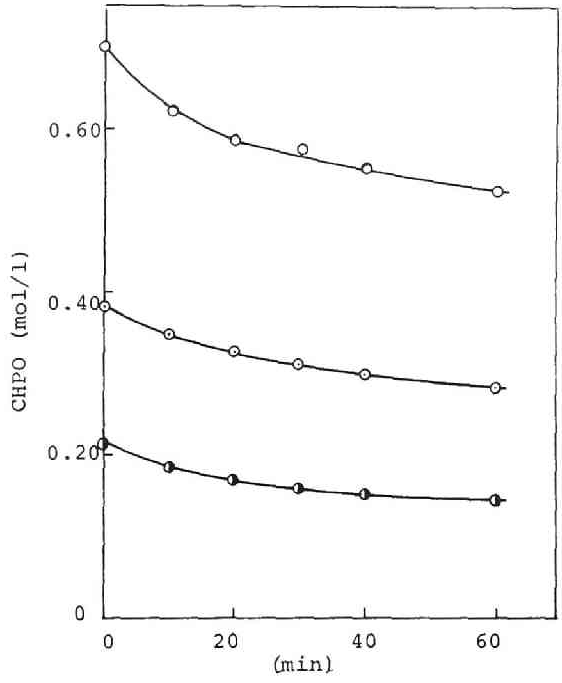


Fig. 2 Decomposition of CHPO catalyzed by CuCl in pyridine at 0°C
[CuCl] : 2.7×10^{-2}mol/l

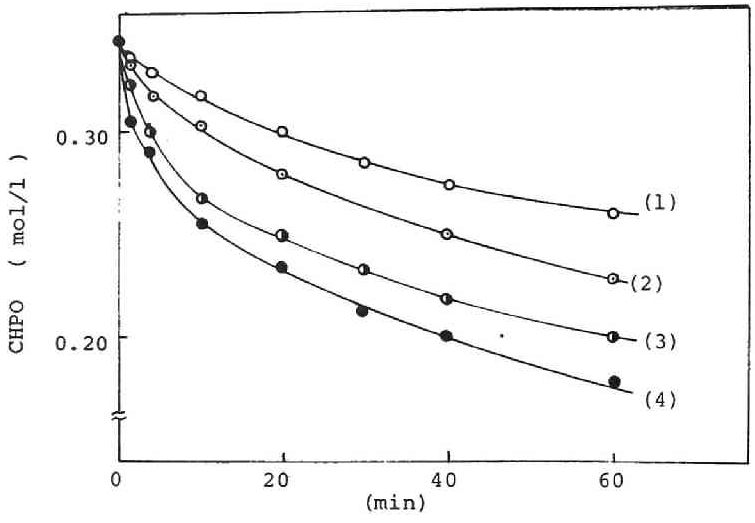


Fig. 3 Decomposition of CHPO catalyzed by CuCl in acetonitrile at $0^{\circ}C$

[CuCl](mol/l)— (1) 2.0×10^{-3} (2) 4.0×10^{-3}
(3) 8.0×10^{-3} (4) 1.6×10^{-2}

CHPO (mol/l)

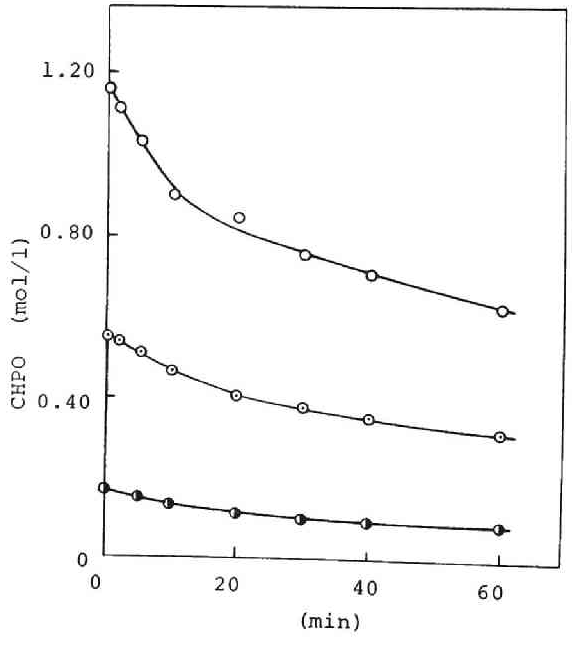


Fig. 4 Decomposition of CHPO catalyzed by CuCl in acetonitrile at $0^{\circ}C$
[CuCl] : 1.6×10^{-2} mol/l

be noted that the decomposition of CHPO catalyzed by copper(I) chloride follows pseudo first order kinetics as shown below:

In pyridine : $-d[CHPO]/dt = k[Cu]^{0.95}[CHPO]^{1.00}$

In acetonitrile : $-d[CHPO]/dt = k[Cu]^{1.02}[CHPO]^{0.80}$

If we assume the radical mechanism presented by Kochi (Eqs, 1 ~ 3)[1], the observed kinetics are consistent with it; that is, if Eqs. 2 and 3 are considered to be rapid compared to the rate-limiting reduction of CHPO by copper(I) chloride (Eq. 1), the rate will depend on $[Cu(I)]^1$ and $[CHPO]^1$ respectively.

Decomposition by copper(II) chloride Fig. 5 shows the result of the decomposition of CHPO catalyzed by copper(II) chloride at 40°C. We see that the reaction shows an induction period which is more marked at low catalyst concentration region. It is noted that the activity of copper(II) salt is much smaller than that of copper(I) salt; that is, copper(I) decomposed CHPO without any induction period at 0°C, but, in the case of copper(II), induction period appeared even at 40°C. From the result mentioned above, it seems that the rate of the direct decomposition of CHPO by copper(II) species (Eq. 4) is very small or almost negligible. Moreover, the reaction was found to be affected by the presence of oxygen; that is, the catalytic activity of copper(II) chloride was found to be decreased by aging the catalyst solution previously under an atmospheric condition and , under an atmosphere of oxygen, the reaction did not proceed. The result suggests that the reaction is initiated by the trace amount of copper(I) species mixed in copper(II) chloride as an impurity and that, during the induction period, the change from copper (II) to copper(I) will occur.

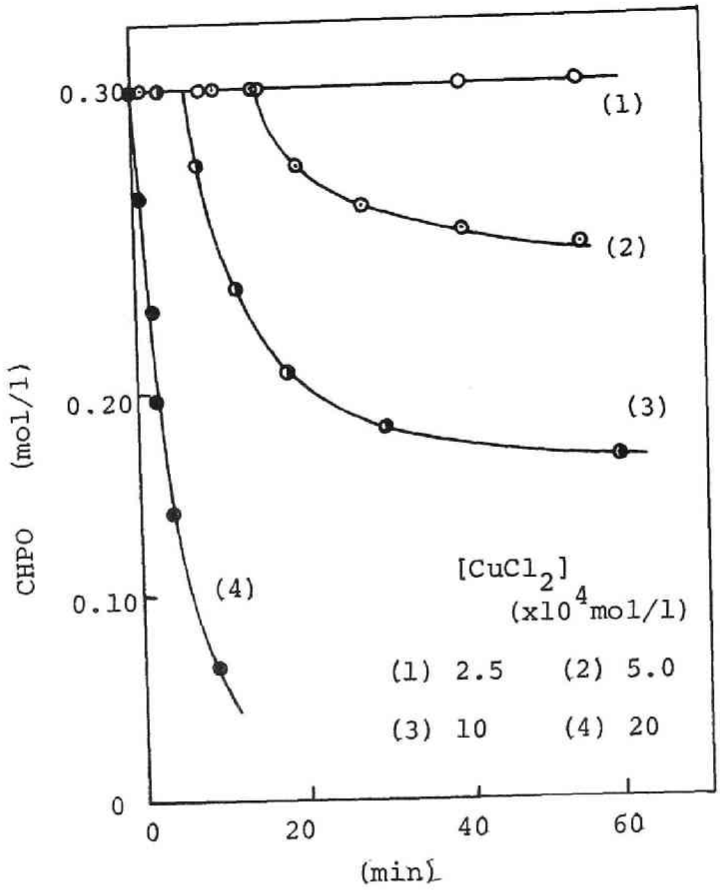


Fig. 5 Decomposition of CHPO catalyzed $CuCl_2$ in pyridine at $40^{\circ}C$

The rate dependence on CHPO concentration is shown in Fig. 6. We see that the increase in the concentration of CHPO results in the elongation of induction period and the decrease in the rate, which could be observed also in acetonitrile. It has been well known that HPO associates in a high concentration region[8], so it may be that the associated CHPO reacted more slowly with copper(II) than free CHPO, which may account for the result shown in Fig. 6. Therefore, the state of CHPO in pyridine was studied by the use of infrared spectra. As can be seen from Fig. 7, I.R. spectrum of CHPO shows the presence of both an associated OH group and a free

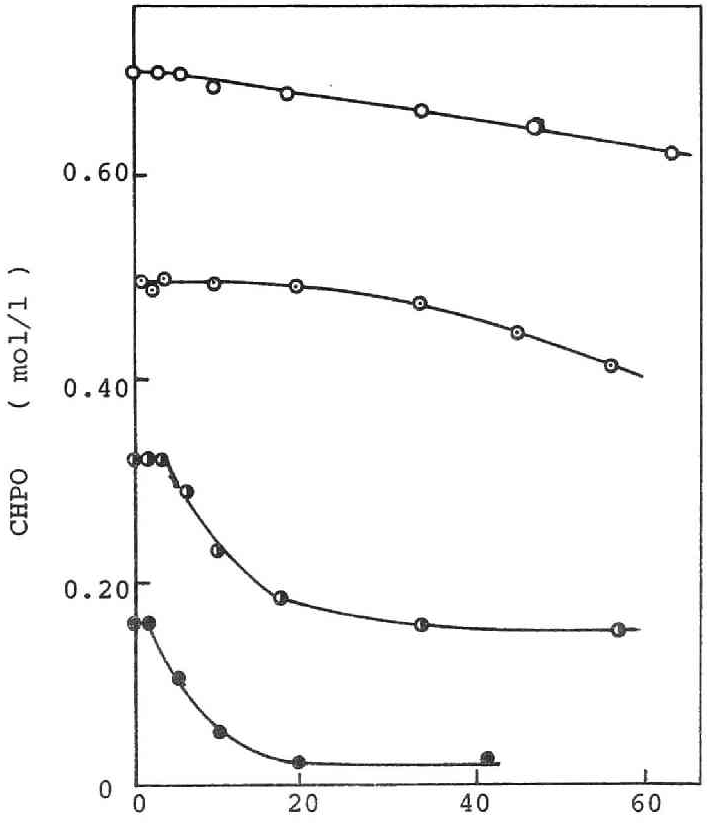


Fig. 6 Decomposition of CHPO catalyzed by $CuCl_2$ in pyridine at 40°C

[$CuCl_2$] : 1.0×10^{-3} mol/l

OH group. However, on addition of pyridine equal amount to CHPO, all of CHPO dissociates and only the absorption by solvated OH is seen. From the result, it is clear that, under the condition employed in this experiment, all of CHPO is solvated by pyridine and that the decrease in the rate of decomposition at high CHPO concentration (see Fig. 6) cannot be attributable to the association of CHPO. Though the phenomenon cannot be elucidated now, one of the explanation may be that an excess CHPO cages copper(II) species and inhibits the interaction of copper(II) with alkyl radical to produce copper(I).

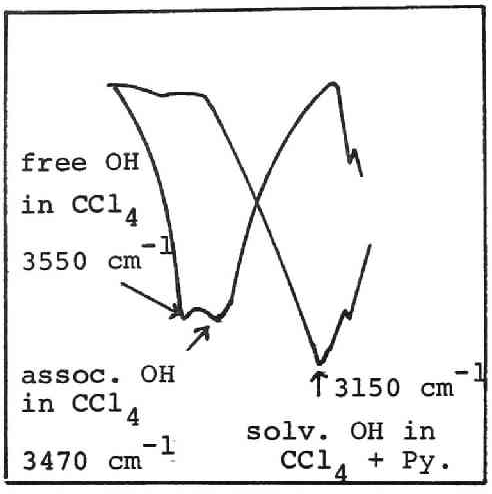


Fig. 7 IR spectra of CHPO in CCl_4
[CHPO]:3.3×10^{-1}mol/l
[Pyridine]:3.3×10^{-1}mol/l

Product distribution Cumyl alcohol, acetophenone and methyl alcohol were obtained as main products in the decomposition of CHPO. In addition, trace amount of α,α'-dipyridyl (about 2%) was obtained, which showed that the hydrogen abstraction by cumyloxy radical from pyridine occurred. In Table 1, the relative distribution of cumyl alcohol and acetophenone is shown. It can be seen that, in the case of copper(II) chloride, the yield of alcohol is about 60% and that of acetophenone is 40%. On the other hand, the decomposition by copper(I) chloride produces 75% of alcohol and 25% of acetophenone. This discrepancy in the product distribution between these two cases seems to be due to the difference in the reaction temperature; that is, it was reported that, as a reaction temperature was lowered, the abstraction of hydrogen by alkoxy radical to produce alcohol predominated over fragmentation.[9] In fact, at 40°C, the product distributions in both cases coincided with one another. (see the last run in Tavle 1)

Table 1 product distribution

Solvent : Pyridine 40°C

Catalyst ($\times 10^3$ mol/l)		CHPO (x10mol/l)	Temp (°C)	Aceto-phenone (%)	Cumyl alcohol (%)
$CuCl_2$	2.0	1.28	40	44.6	55.4
	2.0	1.70	40	38.9	61.1
	2.0	2.22	40	42.4	57.6
	2.0	2.55	40	39.1	60.9
	2.0	3.40	40	40.5	59.5
	3.0	3.40	40	39.3	60.7
	4.0	3.40	40	42.0	58.0
	2.0	5.10	40	43.7	56.3
CuCl	9.6	1.70	0	22.6	77.4
	2.7	1.70	0	26.1	73.9
	2.0	3.40	0	25.0	75.0
	8.0	3.40	0	25.8	74.2
	2.7	3.40	0	24.7	75.3
	3.2	3.40	40	45.7	54.3

Only 6ml/0.014 mol.CHPO of gaseous products were found to be produced, which shows that oxygen was scarcely produced and that the direct decomposition of CHPO by copper(II) chloride (Eq. 4) did not play an important role during the reaction.*

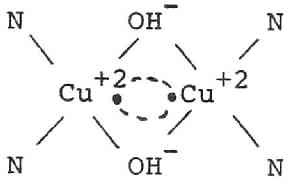
Change of the catalyst system during the reaction

As can be seen from Fig. 8, ESR spectrum of copper(II) chloride in pyridine shows an asymmetric form due to square planar complex with seven to ten peaks near the center, which suggests that pyridine coordinates to copper. (see Chapter 1) During the induction period, the spectrum

---

* A gas bullete was attached to the reaction vessel and the quantity of evolved gaseous products were measured by the increase of a volume of the gas bullete. If a half of CHPO is decomposed by copper(II) to produce ROO· radical (Eq. 4), about 157 ml of oxygen would be obtained. The composition of these gaseous products was not analyzed.

shows no change but, as the reaction proceeds, it becomes broad and super-hyperfine signal becomes indistinct. After the reaction at which the catalyst became deactivated and precipitated, no signal could be seen. As copper(II) ion is known to dimerize through OH^- ion in basic solvent,[10] it seems that the deactivated catalyst has a dimer structure as shown below:



By the quenching of the spin moment in this way, the ESR signal due to copper(II) ion would disappear.

Visible spectrum of the reaction mixture showed an absorption at 730 nm due to copper(II)-pyridine complex at the beginning of the reaction, but, at the later stage, owing to the precipitation of the catalyst, we could

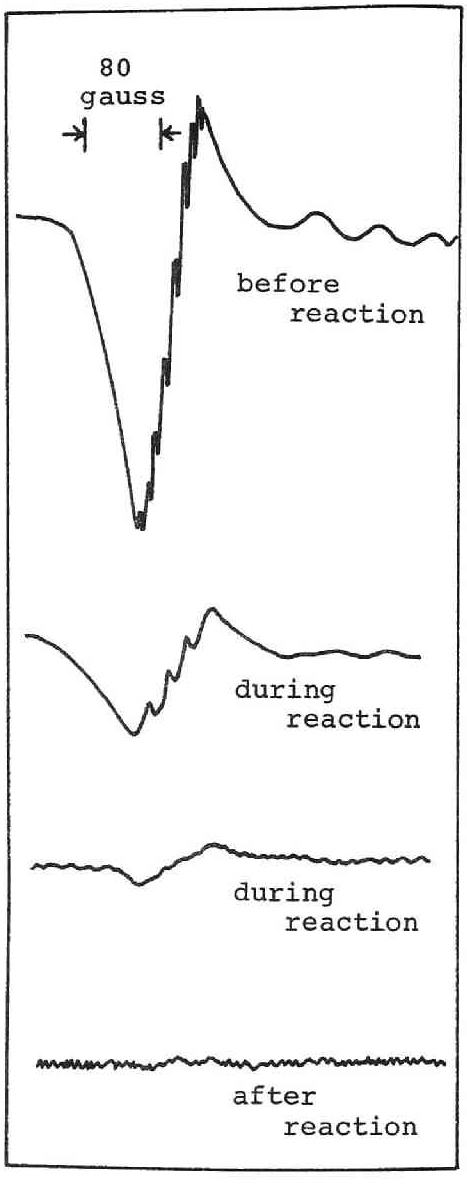


Fig. 8 ESR spectrum of the catalyst system in pyridine at 40°C

[CHPO] : 3.4×10^{-1} mol/l
[$CuCl_2$]: 5.0×10^{-4} mol/l

Spectra were measured at -196°C

not obtain any information.

Discussion concerning the induction period

As stated earlier, copper(II) chloride was much less active than copper(I) chloride and lost its activity in the presence of oxygen where the change from copper(II) to copper(I) was inhibited. These results shows that the rate of the direct decomposition of CHPO by copper(II) (Eq. 4) is very small, which seems to cause an induction period. Here, we have studied the effect of various additives on the induction period, that is, on the change from copper(II) to copper(I) and the result is summarized in Table 2. We see that an induction period disappears or shortened by the addition of such inhibitors as α-naphthyl amine, β-naphthol or hydroquinone. (run 2∼5) It seems that these inhibitors act rather as radical producers than as radical traps and that the radicals from these substances interacts with copper(II) to form active copper(I) species. This is also proved from the experiment using AIBN, a radical initiator. (run 6)

$$\text{Inhibitor} \atop \text{Initiator} \longrightarrow R\cdot \xrightarrow{Cu^{+2}} Cu^{+1} + R^{+}$$

Hydroquinone, a reducing agent as well as an inhibitor, may reduce copper(II) to copper(I). Cumyl alcohol or acetophenone, which is an impurity mixed in CHPO, has no effect.(runs 7 and 8) Alkali chlorides which activated copper catalyst in the decomposition of hydroperoxide in acetic acid[11] have little or rather retarding effect. (runs 9∼11) Bromine, an oxidizing agent, inhibits the reaction probably by the oxidation of copper (I) to copper(II) state (run 16), as in the case of oxygen. Hexamethylphosphoric triamide (HMPA) and water which produces OH^{-} ion in pyridine both inhibited the reaction.(runs 14 and 15) These reagents seem to coordinate to copper and prevent reactants from approaching the coordination sphere of copper. From these results,

Table 2 Effect of additives

[CHPO] : 3.40×10^{-1} mol/l

[$CuCl_2$] : 5.0×10^{-4} mol/l

Solvent : Pyridine 40°C

run	Additives (2.0×10^{-2} mol/l)	Induction period (min)
1	None	16
2	Hydroquinone	0
3	α-Naphthylamine	0
4	β-Naphthol	0
5	Phenol	1
6	AIBN	4
7	Cumyl alcohol	15
8	Acetophenone	16
9	NaCl	14
10	KCl	14
11	LiCl	>60
12	Na_2SO_3	>60
13	LiBr	0
14	H_2O	>60
15	HMPA	>60
16	Br_2	>60

it is clear that the reaction is initiated after copper(I) species is formed and that, during the induction period, the change from copper(II) to copper(I) occurs.

According to Kochi's theory, copper(I) ion was considered to be produced by the reaction of copper(II) with alkyl radical which was formed by the thermal decomposition of peroxide during the induction period. Therefore, we have carried out the thermal decomposition of CHPO in our experimental condition and an Arrhenius plot is shown in Fig. 9. An apparent activation energy was found to be 43.0 kcal/mol and, from this, the rate of the thermal

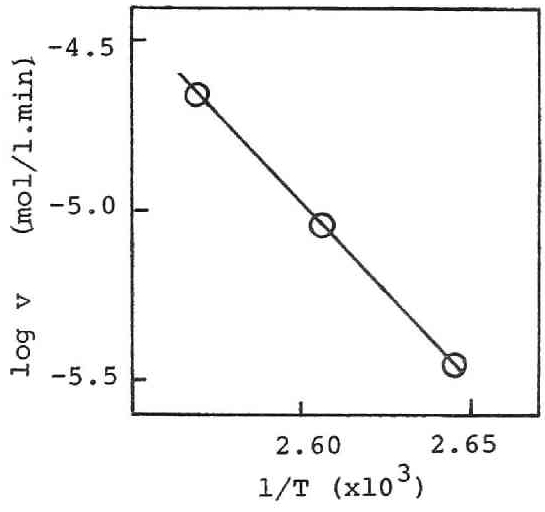


Fig. 9 Arrhenius plots for the thermal decomposition of CHPO in pyridine

[CHPO] : 3.40×10^{-1} mol/l

decomposition at 40°C was obtained as 3.0×10^{-11} mol/l.min. If all of the decomposed CHPO produce alkyl radical on fragmentation and reduce copper(II) to copper(I) state, the amount of copper(I) produced during the induction period is less than 4.8×10^{-10} mol/l. It seems improbable that such a trace amount of copper(I) can initiate the decomposition of CHPO.

In Fig. 10, the effect of copper(I) chloride on the induction period is shown. [$CuCl_2$: 5.0×10^{-4} mol/l, CHPO : 0.34 mol/l] We see that at least 1×10^{-7} mol/l of copper(I) is necessary to initiate the decomposition.

From the result given in Fig. 10, it seems that, in the decomposition of a stable HPO such as CHPO, copper(I) cannot be formed during the induction period by the reaction between copper(II) and the intermediate radical formed in the thermal decomposition of CHPO.

As stated earlier, the direct decomposition of CHPO by copper(II) (Eq. 4) was negligible at the later stage of the reaction. However, considering the result

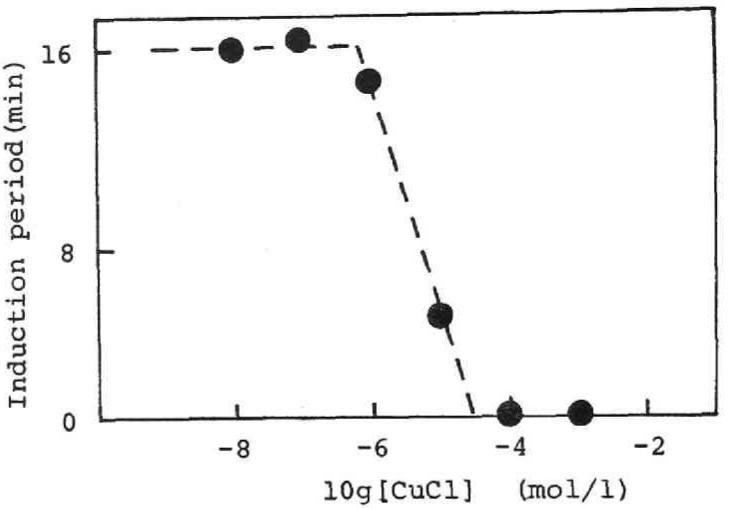


Fig. 10 Effect of CuCl on the induction period of the reaction in pyridine at 40°C
$[CuCl_2]$:5.0x10^{-4}mol/l [CHPO]:3.40x10^{-1}mol/l

obtained in this section, it cannot be ruled out at all during the initial stage of the decomposition, or induction period. Because, if it does occur during the induction period, the amount of oxygen evolved is only 9 x 10^{-5} ml, which is incapable to analyze, and at the later stage, the rapid reaction of the oxidation of alkyl radical by copper(II) (Eq. 3) would predominate over reaction 4.

Summary

Decomposition of α,α'-dimethylbenzyl hydroperoxide (CHPO) catalyzed by copper chlorides was carried out in pyridine.

Decomposition by copper(I) proceeded without any induction period at 0°C. The rate expression, $-d[CHPO]/dt = k[Cu(I)]^{0.93}[CHPO]^{1.0}$, was obtained and it was in good agreement with the assumed mechanism in which copper(I) initiated the reaction.

On the other hand, induction period appeared even at 40°C in the decomposition by copper(II) chloride. It

was found that the induction period disappeared by the addition of such compounds as reducing agents or radical initiators which reduced copper(II) to copper(I) and was prolonged by adding oxidizing agents which oxidized copper(I) to inactive copper(II). Based on these findings, it was concluded that the transformation from copper(II) to copper(I) state occured during the induction period.

As CHPO exhibited adequate thermal stability under our experimental conditions, it was assumed that copper(I) could not be formed during the induction period by the reaction of copper(II) with the intermediate radical produced in the thermal decomposition of CHPO. Therefore, the possibility of the direct decomposition of CHPO by copper(II) cannot yet be ruled out during the induction period.

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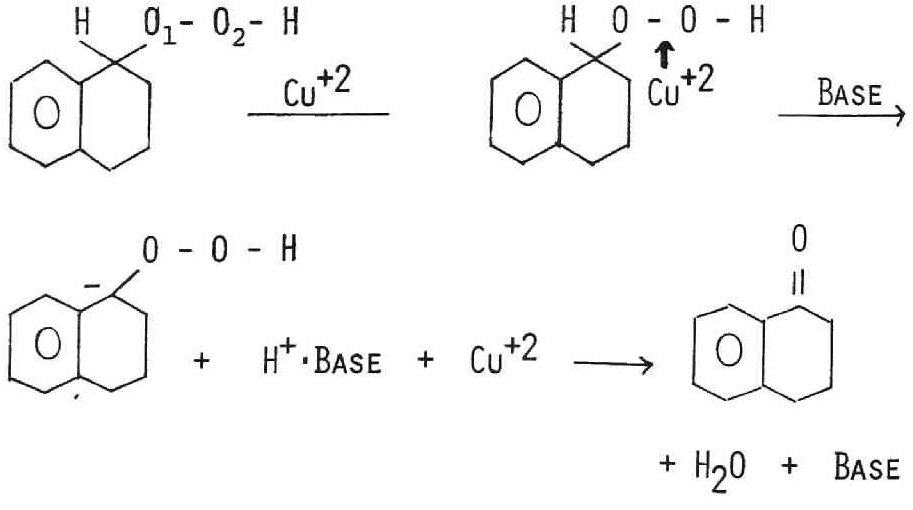
Chapter 3 Decomposition of Benzyl Hydroperoxide Catalyzed by Copper Chlorides in Pyridine

Introduction

Catalytic decompositions of primary and secondary hydroperoxides (HPO) by metal salts have been carried out by a number of investigators.[1~6] However, discussions for the catalysis in the decomposition of primary HPO have, owing to the complexity of the reaction, scarcely been given.[7~9]

Previously, we have investigated the catalysis of copper chlorides in the decomposition of 1,2,3,4-tetrahydro-1-naphthyl HPO (THPO) and α,α'-dimethylbenzyl HPO (CHPO) and found that the decomposition of CHPO (tertiary HPO) catalyzed by copper(I) and copper(II) chlorides and that of THPO (secondary HPO) catalyzed by copper(I) chloride proceeded in a radical mechanism. However, it was considered that copper(II) chloride also promoted an ionic dehydration of THPO in basic solvents; in which copper(II) attacked oxygen atoms of THPO followed by the abstraction of α-hydrogen by base as shown below:*



In this chapter, we have studied the catalytic activity of copper chlorides in the decomposition of benzyl

HPO (primary HPO) which has two α-hydrogen atoms in pyridine and the result was compared with those obtained in the previous chapters.

Experimental

Material Benzyl HPO (BHPO) was obtained as follows.[10] Benzyl magnesium chloride (Grignard reagent) was prepared from benzyl chloride and magnesium metal and 0.2 mol of the reagent was diluted with ethyl ether to 0.5 N. Adding 0.21 mol of cadmium chloride to this solution at 0°C, magnesium was replaced by cadmium and to this solution dried oxygen was bubbled for about 1 hr at -70°C. Then 0.1 N aqueous sulfuric acid was added dropwise to this reaction mixture followed by the extraction with ethyl ether. BHPO was again extracted with cold 2% aqueous sodium hydroxide as sodium salt and, to this, CO_2 gas was bubbled to liberate BHPO. BHPO was extracted with ethyl ether and ethyl ether was removed under reduced pressure. BHPO so obtained was stored in the dark place. Benzyl nitrite was obtained from benzyl alcohol and sodium nitrite by the method described by Noyes.[11] Crude benzyl nitrite was distilled twice under reduced pressure and stored in the dark place. (b.p 59.5 ~ 60.5°C/12mmHg) Pyridine or other solvents were purified by standard methods. Copper (I) chloride was obtained by the reduction of copper(II) dihydrate.[12] Other reagents (GR grade) were used without further purification.

Apparatus and procedure Apparatus used and procedures in the decomposition of BHPO or other hydroperoxides were the same as described in the previous chapters. Photo-decomposition of benzyl nitrite was carried out using a reactor equipped with a 200 W high pressure mercury lamp

* The direction of the attack of copper salt (O_1 or O_2) was not clarified.

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Analytical procedures The reaction products were identified by gas chromatography. (Column : PEG 1000 1m, Column temperature : $80^{\circ}C \sim 150^{\circ}C$ ($5^{\circ}C$/min), Carrier gas : N_2 30 ml/min)

Result and Discussion

Decomposition by copper(I) chloride Fig. 1 and Fig. 2 show the results obtained in the decomposition of BHPO catalyzed by copper(I) chloride in pyridine.

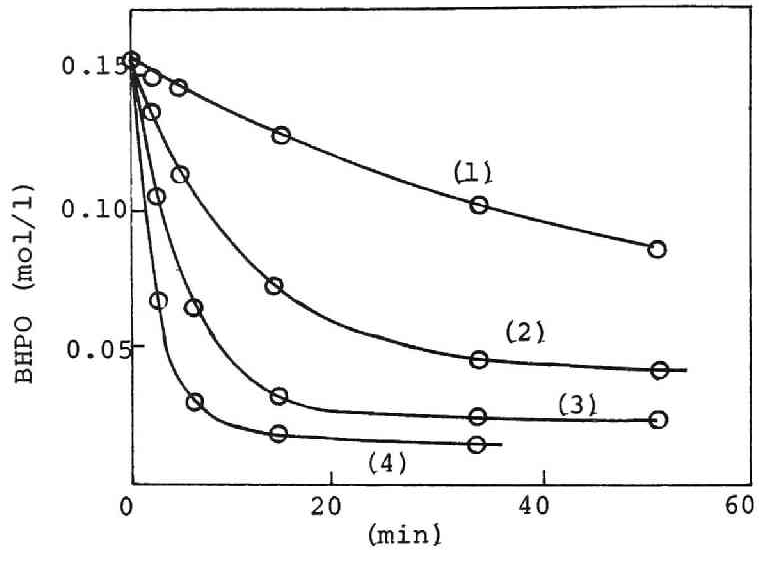


Fig. 1 Decomposition of BHPO catalyzed by CuCl in pyridine at $-20^{\circ}C$
[CuCl] ($\times 10^{4}$ mol/l) – (1) 2.0 (2) 5.0 (3) 10 (4) 20

We see that the reaction proceeds without any induction period at $-20^{\circ}C$, which shows that copper(I) has high activity and promote the direct decomposition of BHPO. Initial rate of the decomposition was found to be expressed as

$$-d[BHPO]/dt = k[CuCl]^{1.20}[BHPO]^{1.09} \qquad (1)$$

From the results obtained in the previous chapters, rate

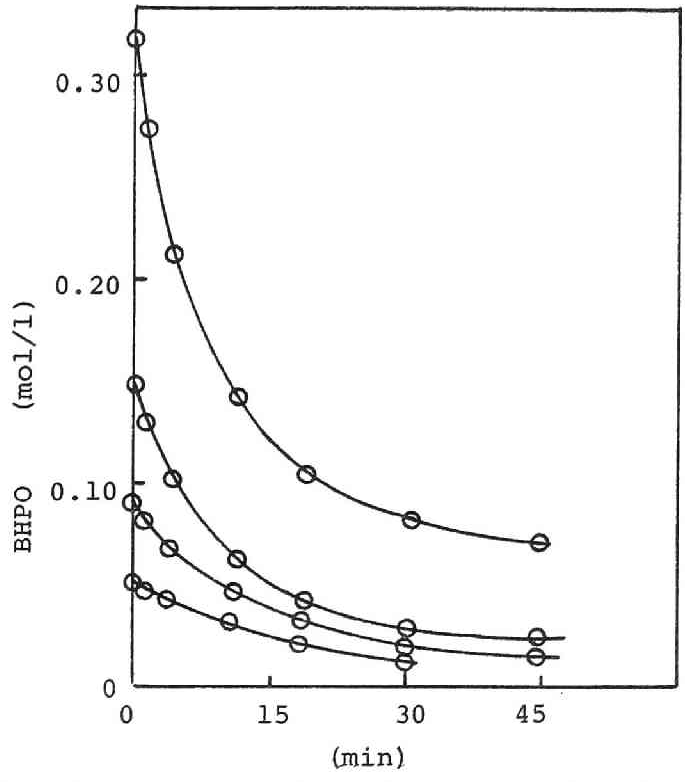


Fig. 2 Decomposition of BHPO catalyzed by CuCl in pyridine at -20°C

[CuCl] 5.0 x 10^{-4}mol/l

expressions for the decomposition of CHPO or THPO were obtained as

$$-d[THPO]/dt = k[CuCl]^{1.05}[THPO]^{1.01} \qquad (2)^{**}$$

$$-d[CHPO]/dt = k[CuCl]^{0.93}[CHPO]^{1.00} \qquad (3)$$

Eqs. (1) ~ (3) show that the decomposition of primary (BHPO), secondary (THPO) and tertiary (CHPO) hydroperoxides catalyzed by copper(I) all proceed in the same radical mechanism. By the radical mechanism (Eqs. 4 ~ 6), in which step (4) is an initiating and rate determining

** The rate dependence on THPO concentration was obtained in this work.

one[13], rate expression for the decomposition of HPO is obtained (Eq. 7), which is in good agreement with the observed kinetics shown above.

$$ROOH + Cu^{+1} \longrightarrow RO\cdot + OH^{-} + Cu^{+2} \quad (4)$$

$$RO\cdot \longrightarrow R''{=}O + R'\cdot \quad (5)$$

$$R'\cdot + Cu^{+2} \longrightarrow R'^{+} + Cu^{+1} \quad (6)$$

$$-d[HPO]/dt = k[CuCl]^{1}[HPO]^{1} \quad (7)$$

Decomposition by copper(II) chloride under a nitrogen atmosphere

Decomposition curves of BHPO catalyzed by copper(II) chloride under a nitrogen atmosphere are shown in Figs. 3 and 4. As can be seen from the figures, a retardation period appears at the beginning of the reaction, especially remarkable at low catalyst concentration region. After the retardation period, the rate of the decomposition increases. This acceleration of the reaction seems to be due to the accumulation of active copper (I) species; that is,

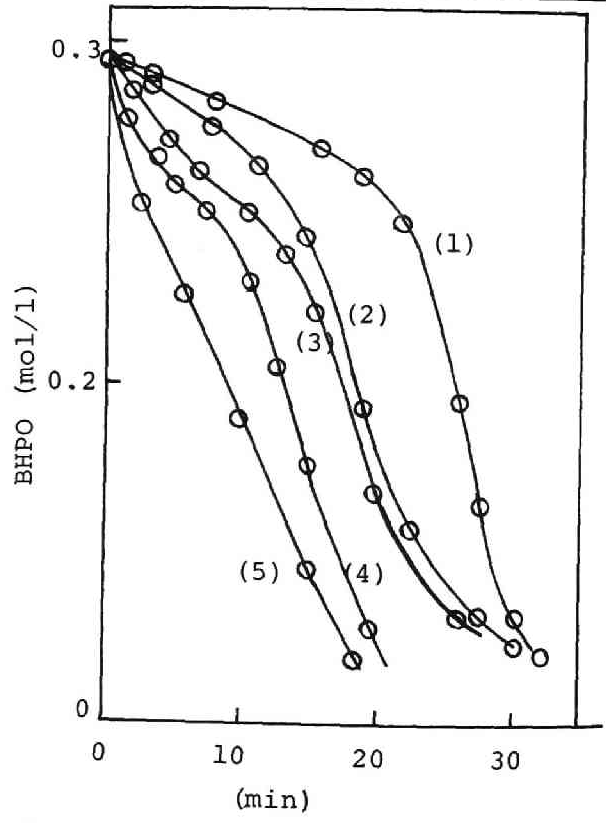


Fig. 3 Decomposition of BHPO catalyzed by $CuCl_2$ in pyridine at 35°C N_2 atmosphere
$[CuCl_2]$ ($\times 10^4$ mol/l) – (1) 5.0 (2) 10 (3) 20 (4) 40 (5) 80

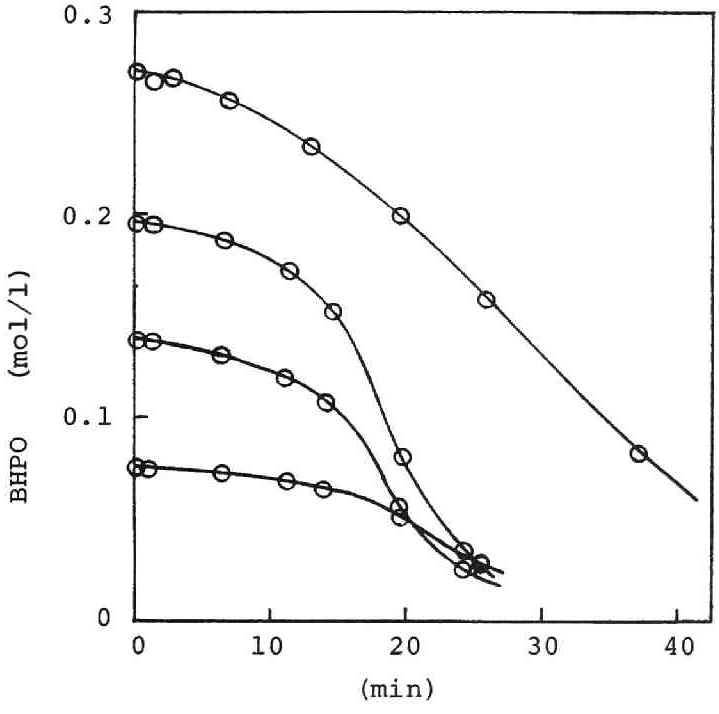


Fig. 4 Decomposition of BHPO catalyzed by $CuCl_2$ in pyridine at 35°C
$[CuCl_2]$ 1.0×10^{-3} mol/l N_2 atmosphere

during the retardation period, radical is produced by the thermal decomposition of BHPO*** and reacts with copper(II) to produce active copper(I) species. (see the discussion in Chapter 2) After the retardation period, the decomposition seems to proceed by the radical reactions, (4)~(6), as in the case of copper(I) chloride.

Effect of oxygen In the radical decomposition of CHPO, the reaction was found to be retarded remarkably by oxygen which oxidized active copper(I) to copper(II) state.

*** As the rate constant of the thermal decomposition of BHPO at 40°C was found to be considerably large ($1.17 \times 10^{-4} min^{-1}$), enough amount of copper(I) to initiate the reaction will be produced during the retardation period. (see Chapter 2)

On the other hand, ionic dehydration of THPO by copper(II) was not affected by oxygen so much. Therefore, it seems useful to discuss the effect of oxygen for the elucidation of the mechanism of this reaction (radical or ionic). In Fig. 5, the effect of oxygen is shown. We see that the rate is highly decreased in the presence of only 5% of oxygen which shows that the radical reaction under a nitrogen atmosphere (curve 1 in Fig. 5) is retarded by the transformation of active copper(I) to copper(II). However, more than 5% of oxygen has no further effect upon the rate (curves 3～5).

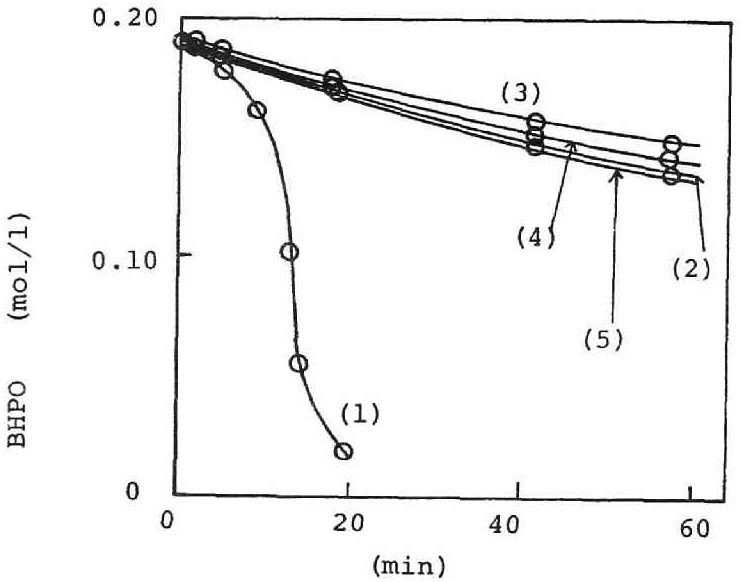


Fig. 5 Decomposition of BHPO catalyzed by $CuCl_2$ in pyridine at 35°C Effect of O_2
$[CuCl_2]$ 1.0×10^{-3} mol/l Partial pressure of O_2 – (1) 0 (2) 0.05 0.20 (3) 0.60 0.80 (5) 1

Figs. 6 and 7 show the rate dependences on copper(II) and BHPO concentrations in the presence of 20% of oxygen, that is, under an atmospheric condition. It can be seen that, in all cases, decompositions proceed slowly but without any induction period, indicating that copper(II) is active for the initiation of the reaction. The rate

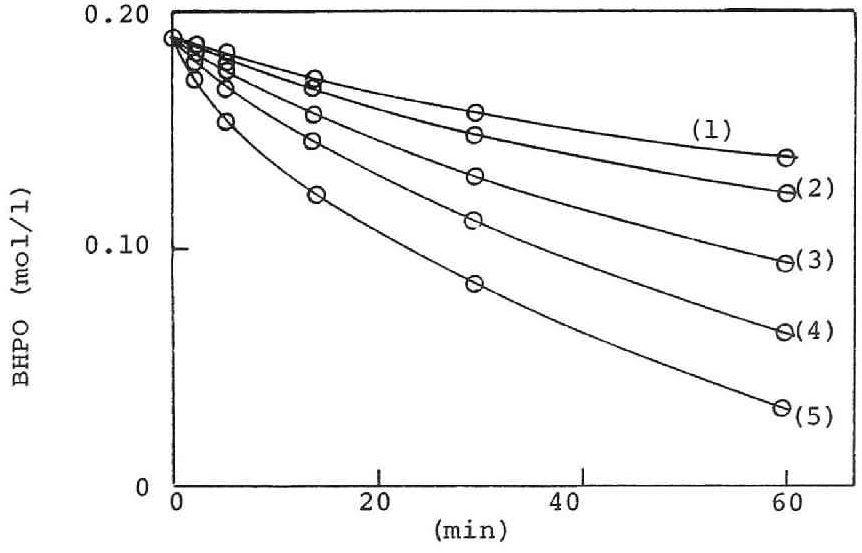


Fig. 6 Decomposition of BHPO catalyzed by $CuCl_2$ under an atmospheric condition in pyridine at 35°C
$[CuCl_2]$ ($\times 10^4$ mol/l) (1) 5.0 (2) 10 (3) 20 (4) 40 (5) 80

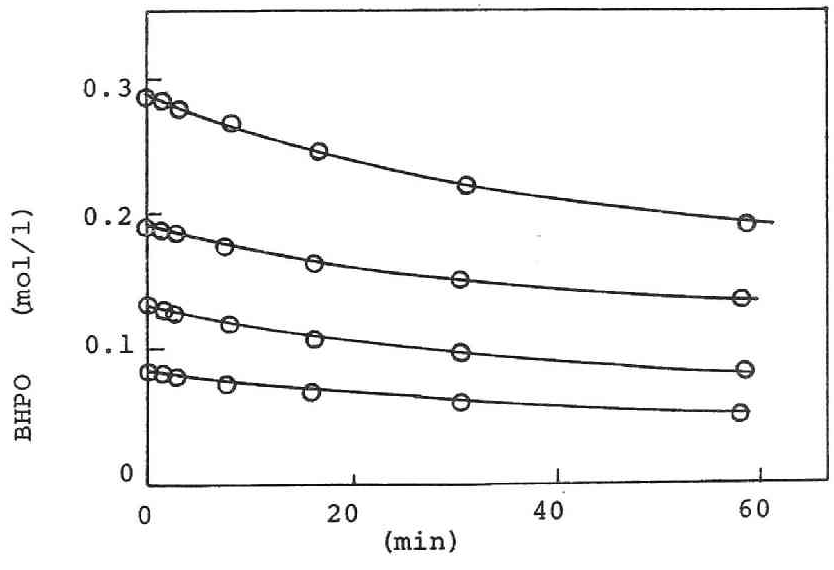


Fig. 7 Decomposition of BHPO catalyzed by $CuCl_2$ under atmospheric condition in pyridine at 35°C $[CuCl_2]$ 1.0×10^{-3} mol/l

expression is obtained as follows:

$$-d[BHPO]/dt = k[CuCl_2]^{1.12}[BHPO]^{1.02} \qquad (8)$$

This rate dependence and the decomposition curves (Figs. 6 and 7) under an atmospheric condition resembles to those in the ionic dehydration of THPO. Therefore, it seems that when the formation of copper(I) is inhibited by oxygen, BHPO which has, like THPO, α-hydrogen atoms is decomposed in an ionic dehydration by copper(II) - pyridine system.

The initial rate of the decomposition of BHPO under a nitrogen atmosphere was compared with that under an atmospheric condition. It can be seen from Fig. 8 that the initial rates lie almost on the same line in both cases, , which suggests that the decomposition of BHPO under a nitrogen atmosphere also proceeds mainly in an ionic dehydration at the beginning of the reaction where an accumulation of active copper(I) is inadequate.

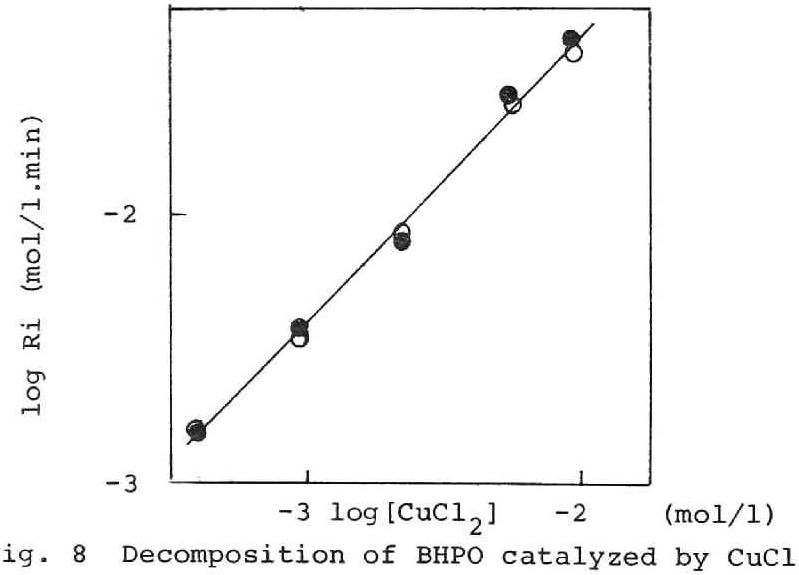


Fig. 8 Decomposition of BHPO catalyzed by $CuCl_2$ in pyridine [BHPO] 0.192 mol/l
○ under an atmospheric condition
● under a nitrogen atmosphere

Effect of water Previously, we have described that the addition of water exhibited an accelerating effect on the ionic dehydration of THPO catalyzed by copper (II) - pyridine system, in which water was considered to produce OH^- ion, more basic than pyridine and capable of abstracting α-hydrogen of THPO.

In this work, also, the effect of water was studied. Fig. 9 shows that the addition of water retards the catalytic decomposition of BHPO by copper(I) (radical reaction), which is the same phenomenon as in the case of THPO. In the decomposition of BHPO catalyzed by

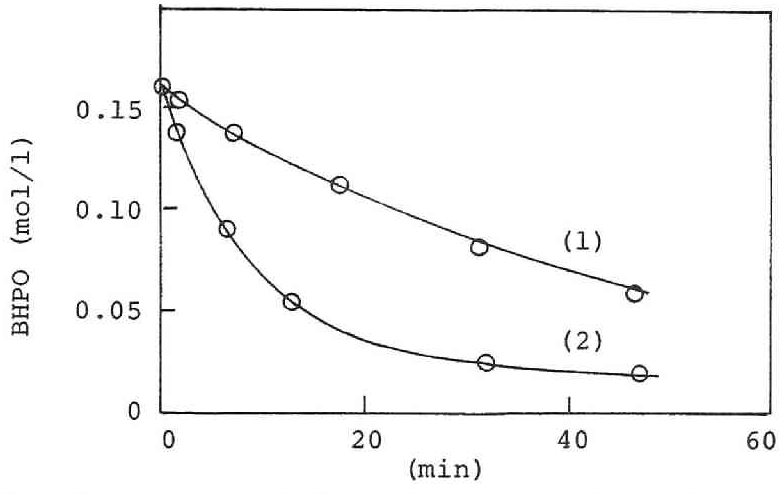


Fig. 9 Decomposition of BHPO catalyzed by CuCl in pyridine at -20°C Effect of O_2
[CuCl] 5.0×10^{-4}mol/l [H_2O](mol/l) (1) 1.39 (2) 0

copper(II) chloride under a nitrogen atmosphere, water accerelates the initial rate but has no effect at the later stage (Fig. 10) and, as shown by the curve (4) in the figure, excess water reatrds the reaction, that is, the acceleration of the reaction disappears.**** On the other hand, water promotes the reaction catalyzed by

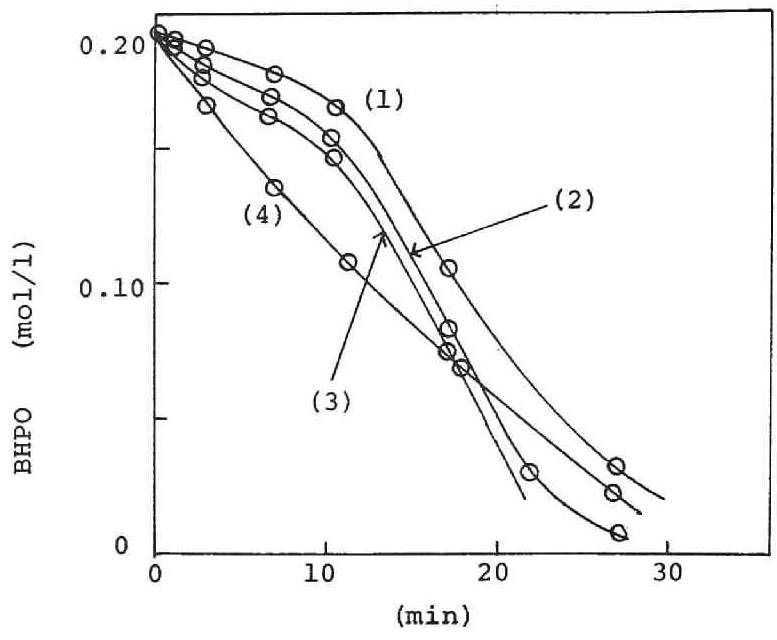


Fig. 10 Decomposition of BHPO catalyzed by $CuCl_2$ in pyridine at 35°C Effect of water N_2 atmosphere $[CuCl_2]$ 1.0×10^{-3} mol/l
$[H_2O]$ (mol/l) (1) 0 (2) 0.79 (3) 1.58 (4) 4.76

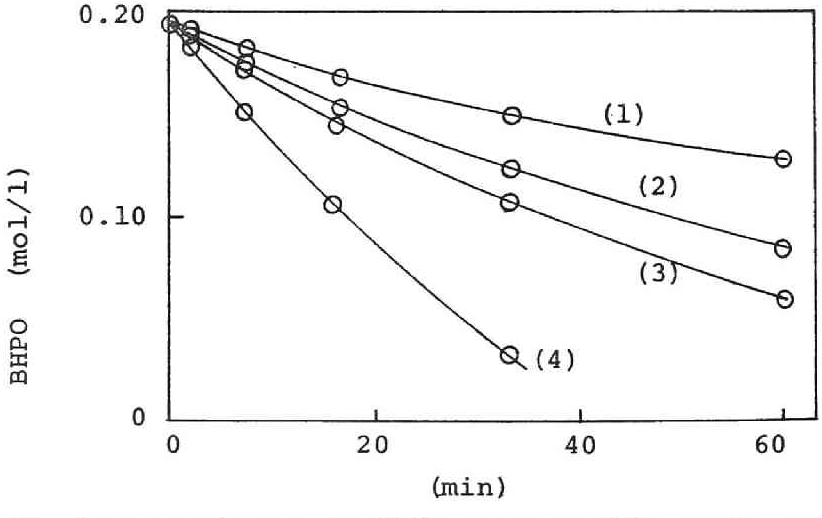


Fig 11. Decomposition of BHPO catalyzed by $CuCl_2$ under an atmospheric condition in pyridine at 35°C
Effect of water $[CuCl_2]$ 1.0×10^{-3} mol/l
$[H_2O]$ (mol/l) (1) 0 (2) 0.79 (3) 1.58 (4) 4.76

copper(II) under an atmospheric condition, from which it is also shown that this reaction proceeds in an ionic process. (Fig. 11)

Product distribution In Table 1, the product distribution in the catalytic and thermal decomposition of BHPO is shown. We see that benzaldehyde and water are almost selectively obtained in the catalytic decomposition. However, in the thermal decomposition, about 10% of benzyl alcohol was obtained in addition to these products.

Table 1 Products of the decomposition of BHPO in pyridine

BHPO (mol/l)	Catalyst (mol/l)		Temp. (^{o}C)	Product(mol/l) ϕCHO	ϕCH_2OH	H_2O
0.192	$CuCl_2$ 2×10^{-3}	air	35	0.186	0	0.187
0.272	$CuCl_2$ 1×10^{-3}	N_2	35	0.272	0	0.237
0.158	CuCl 1×10^{-3}	N_2	-20	0.155	0	0.145
0.317	CuCl 5×10^{-4}	N_2	-20	0.307	0	0.312
0.177	—	air	100	0.155	0.016	0.175
0.177	—	air	110	0.158	0.017	0.162

Discussion concerning ionic dehydration of primary and secondary hydroperoxides From the results obtained so far, it was deduced that BHPO, as in the case of THPO, was decomposed by copper(II) in an ionic dehydration under an atmospheric condition where the formation of copper(I), active for a radical decomposition of BHPO, was inhibited.

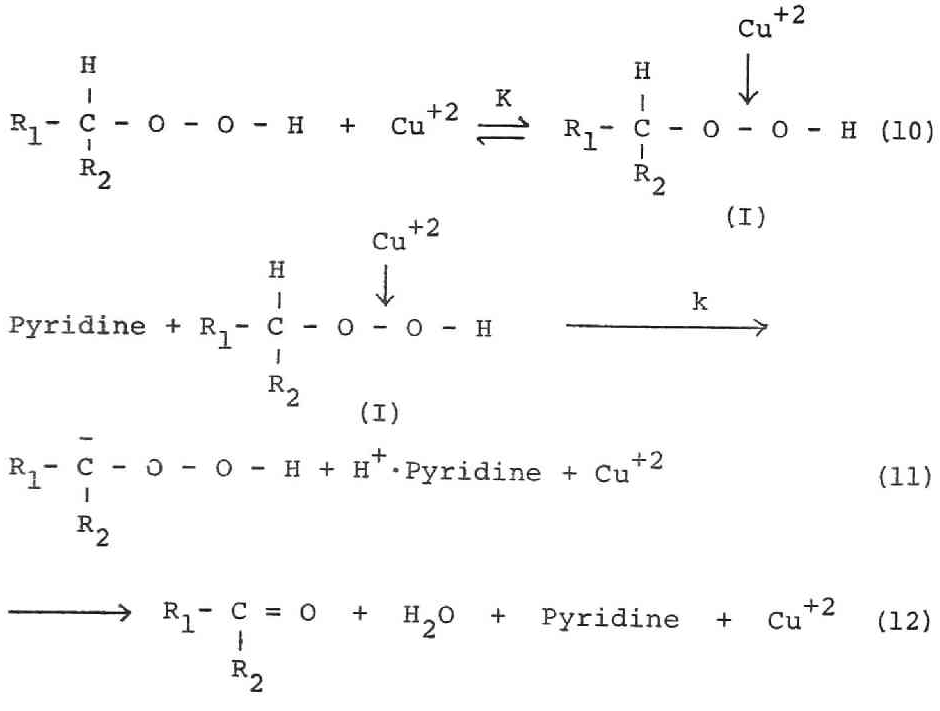
**** In the case of copper(II)-CHPO or copper(I)-THPO systems in which the reaction proceeded in a radical mechanism, water exhibited a retarding effect. (see previous chapter)

Decomposition of cyclohexenyl HPO (secondary HPO) by copper(II) chloride in pyridine was also studied in this work. The rate was found to be proportional to $[Cu(II)]^{1.00}$ and $[\text{Cyclohexenyl HPO}]^{1.00}$ and cyclohexenone and water were selectively obtained, which seems to suggest that cyclohexenyl HPO was decomposed through ionic dehydration.

Therefore, the rate expression for ionic dehydration of primary and secondary hydroperoxides which have α-hydrogen atoms is shown as follows.

$$-d[HPO]/dt = k[Cu(II)]^{1}[HPO]^{1} \qquad (9)$$

Here, we assume the mechanism of the ionic dehydration as follows:



$$R_1\text{-}\underset{\displaystyle R_2}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{-O-O-H} + Cu^{+2} \underset{}{\overset{K}{\rightleftharpoons}} R_1\text{-}\underset{\displaystyle R_2}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{-O-O-H} \quad (10)$$

Cu^{+2} (I)

$$\text{Pyridine} + R_1\text{-}\underset{\displaystyle R_2}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{-O-O-H} \xrightarrow{k}$$

(I)

$$R_1\text{-}\underset{\displaystyle R_2}{\overset{\displaystyle -}{\overset{|}{\underset{|}{C}}}}\text{-O-O-H} + H^{+}\cdot\text{Pyridine} + Cu^{+2} \qquad (11)$$

$$\longrightarrow R_1\text{-}\underset{\displaystyle R_2}{\overset{|}{\underset{|}{C}}}\text{=O} + H_2O + \text{Pyridine} + Cu^{+2} \qquad (12)$$

In the above mechanism, copper(II) attacks the lone pair electrons of HPO and forms complex (I). (Eq. 1) It is assumed that carbon - hydrogen bond of the α-position is weakened by the complex formation. Then pyridine

attacks the α-hydrogen and the reaction proceeds. Step 12 is a rapid reaction involving carbanion and, therefore, cannot be a rate-determining process. On the basis of the mechanism shown above, we assume two cases:

(a) Step (10) is rate-determining. In this cases, the formation of the complex (I) is rate-determining and the rate expression for the disappearance of HPO is expressed as shown below and agrees with the observed one

$$-d[HPO]/dt = k''[Cu]^{1}[HPO]^{1} \qquad (13)$$

mentioned above (Eq. 9).

(b) Step (11) is rate-determining In this case,

$$-d[HPO]/dt = k[Pyridine][\ (I)\ ] \qquad (14)*****$$

The concentrations of HPO and copper(II) which do not form complex (I) are expressed as $[HPO]_f$ and $[Cu]_f$ respectively and that of total concentration as $[HPO]_o$ and

---

***** In the decomposition of cyclohexenyl HPO, the yield of cyclohexenone was increased as the increase of pyridine added. (see Table 4) So the concentration term of pyridine must be involved in Eq. (14).

Table 4 Decomposition of cyclohexenyl HPO catalyzed by $CuCl_2$-pyridine system in cyclohexane at 60°C

Pyridine (mol/l)	Cyclohexenol / Cyclohexenone (mole ratio)
	0.696
1.5×10^{-2}	0.622
3.0×10^{-2}	0.451
3.0×10^{-1}	0.306

$[CuCl_2]$ 8.0×10^{-3} mol/l

N_2 atmosphere

$[Cu]_o$. Then

$$K = \frac{[\ (I)\ ]}{[HPO]_f[Cu]_f} \qquad (15)$$

From this

$$[\ (I)\ ] = K[HPO]_f[Cu]_f = K[HPO]_f([Cu]_o - [\ (I)\ ])$$

$$[\ (I)\ ] = \frac{K[HPO]_f[Cu]_o}{1 + K[HPO]_f} \qquad (16)$$

Substitution of Eq. (16) into Eq. (14) gives

$$-d[HPO]/dt = k[Pyridine]\frac{K[HPO]_f[Cu]_o}{1 + K[HPO]_f}$$

$$= k'\frac{K[HPO]_f[Cu]_o}{1 + K[HPO]_f}$$

When we take the approximation, $[HPO]_f = [HPO]_o$, then

$$-d[HPO]/dt = k'\frac{K[HPO]_f[Cu]_o}{1 + K[HPO]_o} \qquad (17)$$

From Eq. (17), two extreme cases are possible as shown below.

$$-d[HPO]/dt = k'K[HPO]_o^1[Cu]_o^1 \quad \text{when } K[HPO]_o \ll 1$$

$$= k'[Cu]_o^1 \quad \text{when } K[HPO]_o \gg 1$$

We see that the order with respect to the concentration of HPO depends on the equilibrium constant K and varies from zero to one. From the comparison of the observed kinetic with the calculated one (Eq. 9), it seems that the equilibrium shown in step 10 favours almost to the left side, which can be understood considering the equilibrium in such a strong donor solvent as pyridine.

Photo-decomposition of benzyl nitrite As shown previously, benzaldehyde and water were selectively obtained in the radical decomposition of BHPO catalyzed by copper(I)

chloride. This product distribution is the same as that in the ionic dehydration and shows that the basic solvent (pyridine) affects benzyloxy radical formed in a radical decomposition of BHPO. To elucidate the effect of basic solvent, photo-decomposition of benzyl nitrite, which is known to produce benzyloxy radical by U.V. irradiation as shown below, was carried out.

$$RONO \xrightarrow{U.V.} RO\cdot + \cdot NO$$

It can be seen from Table 2 that the yield of benzyl alcohol is high in isopropyl alcohol which has hydrogen atoms to be abstracted easily and that, in chlorobenzene, the yield of alcohol to that of aldehyde is about 1 : 1. In other basic solvents, considerable amount of alcohol is obtained and no correlation can be seen between the yield of aldehyde and Donor Number (D.N) of solvents****** which suggests that basic solvents alone do not increase

Table 2 Photo-Decompn. of Benzyl Nitrite in Various Solvents

0°C N_2 Benzyl Nitrite:0.170M

Solvent	D.N.	Φ CHO (%)	ΦCH_2OH (%)
Pyridine	33.1	33.3	66.7
Dimethyl formamide	26.6	47.3	52.7
THF	20.0	49.5	50.5
Acetonitrile	14.1	83.6	16.4
Isopropyl alcohol		18.8	81.2
Chlorobenzene		49.2	50.8

the yield of aldehyde. However, in the case of the radical decomposition catalyzed by copper(II) under a nitrogen atmosphere, it can be seen from Table 3 that the yield of benzaldehyde is increased in the order, acetonitrile ≒ THF < N,N-dimethyl formamide ≒ dimethyl sulfoxide (DMSO) < pyridine; that is, in the order of the basicity of the solvents. From the results shown in Tables 2 and 3, it seems that copper-basic solvent system, not basic solvent or copper catalyst alone, promotes fragmentation of benzyloxy radical to form benzaldehyde.

Table 3 Products of Benzyl HPO Decompn. in Various Solvents

35°C N_2 $CuCl_2$: 2×10^{-3}M HPO: 0.203M

Solvent	D.N.	ϕ CHO (%)	ϕ CH_2OH (%)
Pyridine	33.1	100	0
DMSO	29.8	96.8	3.2
Dimethyl formamide	26.6	98.3	1.7
THF	20.0	85.3	14.7
Acetonitrile	14.1	88.2	11.8

Therefore, it seems plausible that, in the radical decomposition of BHPO catalyzed by copper salt, benzyloxy radical is caged togather with copper by pyridine (Eq. 18) or that all the reactions (Eqs. 18 and 19) occur in the

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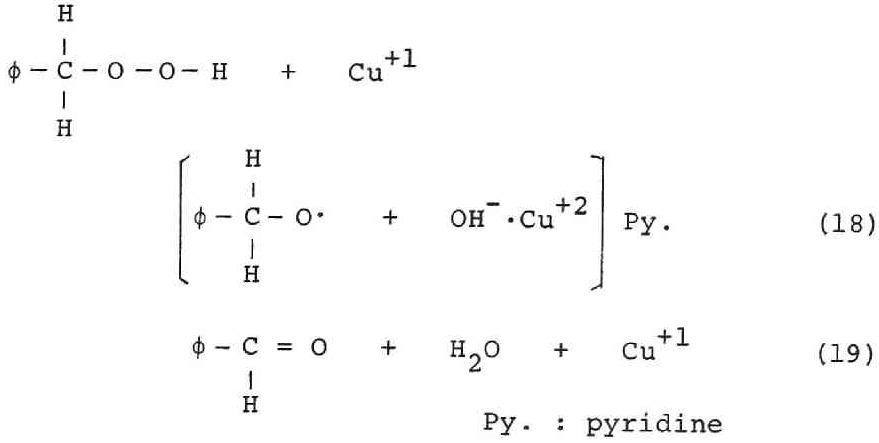
******Donor Number is employed as a measure of basicity of a solvent and defined by the absolute value of the enthalpy change of the following reaction.[14]

$$D + SbCl_5 \rightleftharpoons D\cdot SbCl_5 \quad : -\Delta H$$

D : solvent D.N = $|-\Delta H|$

coordination sphere of copper.



Py. : pyridine

Summary

Decomposition of benzyl hydroperoxide (BHPO) catalyzed by copper chloride was studied in pyridine.

Copper(I) chloride was found to be highly active in the decomposition of BHPO by a radical mechanism.

Copper(II) chloride, not so active as copper(I), also decomposed BHPO by a radical mechanism under a nitrogen atmosphere. However, in the presence of oxygen where the formation of active copper(I) species was inhibited, BHPO was decomposed not by a radical reaction but by an ionic dehydration by pyridine, in which copper (II) was considered to promote the reaction by coordinating to BHPO and weakening its carbon-hydrogen bond of the α-position. The formation constant of this complex was estimated to be considerably small from the kinetic discussion.

Some discussions were also given concerning the behaviour of copper-pyridine system toward the intermediate benzyloxy radical in a radical decomposition.

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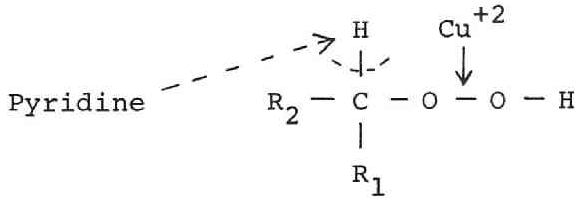
Chapter 4 MO Calculation for an Interaction of Copper and Cobalt Salts with Hydroperoxides

Introduction

MO calculations for an interaction between hydroperoxide (HPO) and transition metals have scarcely been presented.

By the use of the Extended Hückel and the simple Hückel MO method, Yonezawa et al. reported that the decomposition of t-butyl HPO proceeded by the attack of transition metals to the lone pair or anti-bonding orbital of oxygen atom of the HPO.[1] The interaction of methyl HPO with transition metals in the lower valence state (Co(II), Fe(II) and Cr(II)) was also studied using the semi-empirical ASMO SCF method and the Extended Hückel method.[2] However, no calculation has been made for copper salt whose catalytic behaviour in the decomposition of HPO has not yet been clarified fully.[3~6]

Previously, we have studied the catalytic action of copper(II) chloride in the decomposition of primary and secondary HPOs (1,2,3,4-tetrahydro-1-naphthyl, benzyl and cyclohexenyl HPOs) in basic solvent, pyridine, and it was deduced that the reaction proceeded by an ionic mechanism, in which copper(II) was considered to coordinate to the oxygen atom of the HPOs and weaken the carbon - hydrogen bond of the α-position as shown below:



In this chapter, we have discussed the interaction of copper(II) with primary and secondary HPOs by the use of MO calculation to obtain the support for the mechanism of the ionic decomposition of HPO shown above.

The interaction of cobalt(III) salt with HPO was also studied and its mode of action was compared with that of copper(II) salt.

Method of calculation

The semi-empirical SCF-MO method with the CNDO type approximation was used. All valence electrons including the 3d-atomic orbitals of copper were considered explicitly. The molecular orbitals, ψ's, are expressed as linear combination of atomic orbitals. (LCAO approximation)

$$\psi_i = \sum_r C_{ir}\chi_r$$

Where χ_r's are valence atomic orbitals. For a closed-shell molecule, the Roothaan's SCF equation[7] is written as follows:

$$\sum_r C_{ir}(F_{rs} - S_{rs}\varepsilon) = 0$$

$$F_{rs} = H_{rs} + \sum_{tu} P_{tu}[(rs|tu) - 0.5(rt|su)]$$

$$S_{rs} = \int \chi_r \chi_s d\tau$$

$$H_{rs} = \chi_r(\mu) H_\mu^{core} \chi_s(\mu) d\tau_\mu$$

$$(rs|tu) = \iint \chi_r(\mu)\chi_s(\mu)\frac{1}{r_{\mu\nu}}\chi_t(\nu)\chi_u(\nu) d\tau_\mu d\tau_\nu$$

$$P_{tu} = 2\sum_i^{occ} C_{it}C_{iu}$$

In this case, the zero-differential approximation[8] was employed for the overlap integral, S_{rs}, and the electron repulsion integrals, $(rs|tu)$. The one-center and two-center Coulomb repulsion integrals were evaluated by Pariser's and Ohno's approximations respectively.[9, 10] H_{rr} is given by

$$H_{rr} = U_{rr} + \sum_{B\neq A} (B|rr)$$

where an atomic orbital(AO), r, is on the atom A.[11] U_{rr} and $(B|rr)$ represent the interaction energy of an electron in AO with the bare field of its own atom's core and the electrostatic interaction of an electron in AO with the cores of other atoms respectively. These are approximated as follows

$$U_{rr} = -I_r + (rr|rr) - \Sigma^{A}_{s} N_s (rr|ss)$$
$$(B|rr) = -\Sigma^{B}_{t} N_t (rr|tt)$$

where I_r and N_s are the valence state ionization potential of AO, r, and the number of electrons on AO, r, in a neutral atom B respectively. The resonance integral, H_{rs} ($r \neq s$), was calculated by Wolfsberg-Hermholz approximation:[12]

$$H_{rs} = -kS_{rs}(I_r + I_s)$$

where k was taken as 0.5 for the AO pair including d-atomic orbital and 0.4 for the AO pair including only s and p-atomic orbitals. For an atom pair which does not bond with one another, H_{rs} is taken as zero in order to calculate S_{rs}. Slater type orbitals were used for s and p-atomic orbitals and double-ζ type orbital was used only for d-orbital. The value of orbital exponent, I_r[13,14], and $(rr|rr)$[13,14] used in this calculation are listed in Table 1. Two atomic part of the total energy, E_{AB}, proposed by Pople et al.[8] was used as a measure of the strength of the bond between atoms A and B and expressed as

$$E_{AB} = E_{AB}(1) + E_{AB}(2) + E_{AB}(3)$$

where
$$E_{AB}(1) = 2\Sigma^{A}_{r}\Sigma^{B}_{s}(P_{rs}H_{rs})$$
$$E_{AB}(2) = -0.5\Sigma^{A}_{r}\Sigma^{B}_{s}P^{2}_{rs}(rr|ss)$$
$$E_{AB}(3) = \Sigma^{A}_{r}\Sigma^{B}_{s}[(P_{rr} - N_r)(P_{ss} - N_s)(rr|ss)]$$

Copper(II) has d^9 electrons, so the copper-HPO system has an unpaired electron. However, calculations

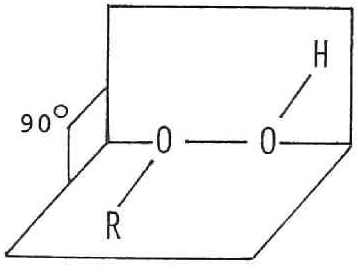
Table 1 Orbital Exponent (ζ), Valence State Ionization Potential (I_r), One-center Coulomb Repulsion Integral (γ_{rr})

Atom	AO	ζ	c*	I_r(eV)	γ_{rr}(eV)
H	1s	1.0000		13.60	12.85
C	2s	1.6083		21.07	12.10
	2p	1.5679		11.27	10.93
O	2s	2.2458		36.07	17.63
	2p	2.2266		18.53	15.13
N	2s	1.9273		26.92	12.87
	2p	1.9170		14.42	11.88
Cl	3s	2.3561		24.02	9.57
	3p	2.0387		15.03	11.30
Cu	3d	5.9500	0.9533	10.85	17.83
		2.3000	0.5744		
	4s	1.5500		7.36	8.25
	4p	1.5500		2.96	6.55

* The double-ζ form was used for the 3d-atomic orbital of copper

were carried out with a closed-shell system and the contribution from an unpaired electron was corrected.

As model compounds for primary and secondary HPOs, methyl and 1-methylallyl HPOs were employed. Square planar $Cu^{+2}(NH_3)Cl_2$ was used as a model catalyst in pyridine and, as a cobalt catalyst, $Co^{+3}(OH)_5$ was employed. Bond lengthes and bond angles of peroxidic group used are shown below and the distance between copper or cobalt and oxygen atom of HPO was taken as 1.95 and 2.22 Å respectively.[15] Other bond lengthes and bond angles were taken from the values in the literature.[15]



ROO = 105°
HOO = 100°
R - O = 1.426Å
O - O = 1.480Å
O - H = 0.970Å

Result

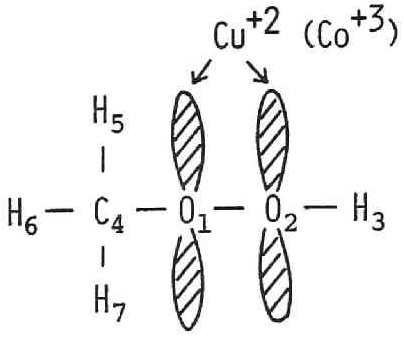
Interaction of $Cu(NH_3)Cl_2$ with methyl HPO (MHPO) and 1-methylallyl HPO (MAHPO) Copper(II) is considered to coordinate to the lone pair orbital of O_1 or O_2 as shown in Fig. 1. Calculations were carried out for the coordination of copper(II) to O_1 and O_2; total energy, E_{total}, the value of E_{AB} and atom population of Cu-MHPO, free MHPO, Cu-MAHPO and free MAHPO are given in Table 2 and Table 3. From the value of E_{total} and E_{Cu-O}, we see that, in both cases, O_1-coordination is preferable to O_2-one, which disagrees with the previous result of Yonezawa who reported that metal ion coordinated to O_2 from the consideration of orbital electron density

Table 2 E_{total}, E_{AB} and Atom Population of MHPO and Cu-MHPO complex

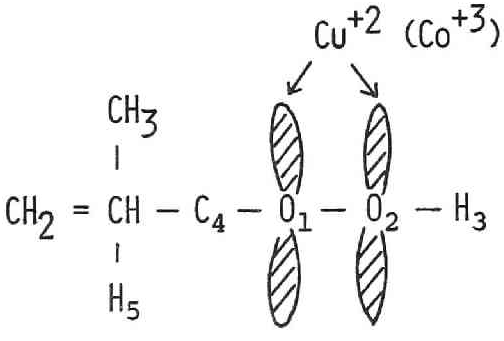
		MHPO	Cu-MHPO complex O_1-coordination	Cu-MHPO complex O_2-coordination
E_{total} (eV)			-3073.68	-2073.48
Atom Population	O_1	6.340	6.321	6.239
	O_2	6.373	6.281	6.365
	H_3	0.642	0.570	0.614
	C_4	3.577	3.635	3.594
	$H_{5,6,7}$ av.	1.023	0.970	0.970
	Cu d		9.269	9.268
	sp		1.972	1.981
$E_{O_1-O_2}$		-14.81	-14.69	-14.23
$E_{O_2-H_3}$		-23.67	-22.94	-22.63
$E_{C_4-H_{5,6,7}}$ av. (eV)		-20.37	-20.21	-20.23
E_{Cu-O_1} or O_2			-12.13	-12.06

Table 3 E_{total}, E_{AB} and Atom Population of MAHPO and Cu-MAHPO complex

		MAHPO	Cu-MAHPO complex	
			O_1-coordination	O_2-coordination
E_{total} (eV)			-3612.50	-3610.26
Atom Population	O_1	6.333	6.310	6.283
	O_2	6.396	6.317	6.417
	H_3	0.647	0.583	0.636
	C_4	3.661	3.736	3.698
	H_5	0.953	1.035	0.981
	Cu d		9.267	8.610
	sp		1.962	2.478
$E_{O_1-O_2}$ (eV)		-14.69	-14.64	-13.61
$E_{O_2-H_3}$ (eV)		-23.77	-23.19	-22.76
$E_{C_4-H_5}$ (eV)		-20.19	-20.10	-20.18
$E_{Cu-O_1 \text{ or } O_2}$ (eV)			-12.40	-12.30



orbital electron density 1.968 1.996



orbital electron density 1.969 1.996

Fig. 1 Orbital electron density on the oxygen of MHPO and MAHPO reacting with copper(II) or cobalt(III)

of free HPO. However, as Cu-HPO complex seems more suitable than free HPO for the discussion of the coordination position, we conclude that O_1-complex is a majour species in the reaction.

It can be seen that O_1-O_2 and O_2-H_3 bonds are weakened and H_3 atom becomes more protic by the complex formation,

Table 4 E_{total}, E_{AB} and Atom population of MHPO and Co-MHPO complex

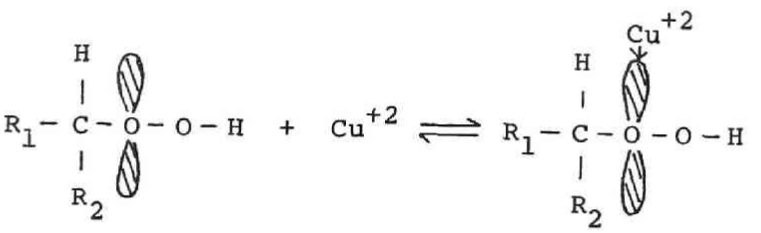
		MHPO	Co-MHPO complex O_1-coordination	Co-MHPO complex O_2-coordination
E_{total} (eV)			-3750.28	-3749.78
Atom Population	O_1	6.340	6.283	6.233
	O_2	6.373	6.290	6.297
	H_3	0.642	0.701	0.613
	C_4	3.577	3.601	3.589
	$H_{5,6,7}$ av.	1.023	0.997	1.050
	Co d		6.663	6.660
	sp		1.380	1.389
$E_{O_1-O_2}$		-14.81	-14.87	-14.94
$E_{O_2-H_3}$		-23.67	-23.51	-22.60
$E_{C_4-H_{5,6,7}}$	av.	-20.37	-20.19	-20.38
$E_{Co-O_1 \text{ or } O_2}$			-10.03	-9.73

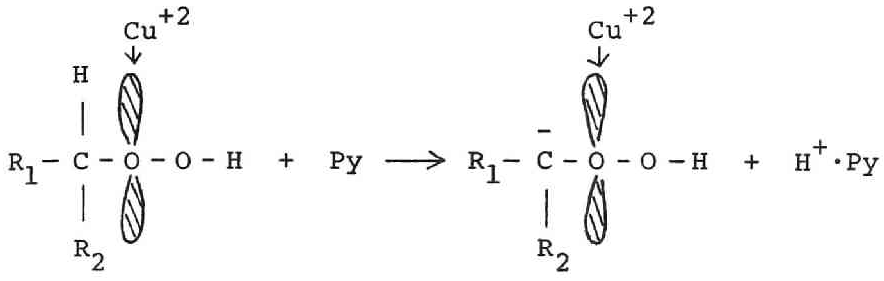
but the degree of the decrease of these values is more remarkable for O_2-coordination. C-H bonds of the α-position are also weakened by the complex formation; in this case, the effect of coordination is larger for O_1 than for O_2.

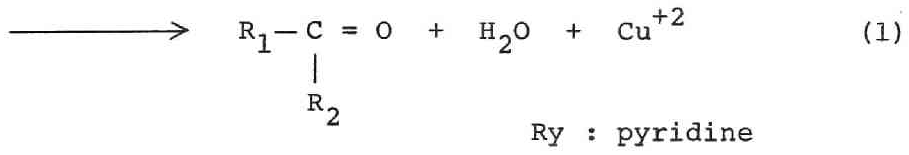
Table 4 shows the effect of coordination of cobalt(III) to MHPO. From E_{total} and E_{Co-O}, O_1-coordination also seems to proceed more easily. The absolute value of $E_{O_1-O_2}$ and $E_{O_2-H_3}$ are decreased and H_3 becomes more protic by the complex formation, but the effect is larger for O_2-coordination. C-H bond of the α-position is also seen to be weakened.

Discussion

Ionic dehydration of primary and secondary HPOs by copper(II) - pyridine system As can be seen from Table 2 and Table 3, C-H bonds of the α-position are weakened by the coordination of copper(II) to O_1, since the absolute value of E_{C-H} is decreased by 0.09~0.16 eV. The result can explain the ionic dehydration of primary and secondary HPOs by copper(II) - pyridine system; that is, copper(II) coordinates to O_1 of HPO through its lone pair orbital and withdraws electron from HPO. In this way, C-H bond of the α-position will be weakened, which suggests that the abstraction of α-hydrogen by pyridine is accelerated by copper(II). The mechanism of the reaction is shown below:







Ry : pyridine

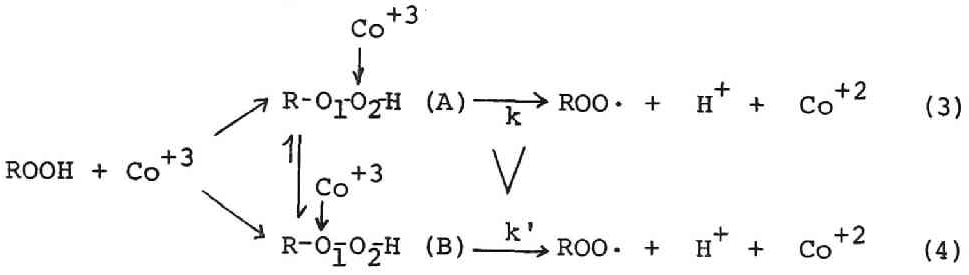
As can be seen from Table 4, cobalt(III) also brings about the decrease in the absolute value of $E_{C-H(\alpha)}$. From this result, it is expected that the ionic dehydration of HPO in basic solvent is accelerated also by cobalt(III). However, owing to the lack of experimental data concerning the catalytic activity of cobalt(III) in pyridine, we could not make any discussions.

Discussion concerning the catalytic behaviour of cobalt(III) and copper(II) in a radical decomposition of HPO Transition metals in their higher valence state are known to decompose HPO by one-electron oxidation of a peroxidic bond to produce peroxy radical and proton:

$$ROOH + M^{+(n+1)} \longrightarrow ROO\cdot + H^{+} + M^{+n} \quad (2)$$

When cobalt(III) coordinates to O_1 or O_2 of MHPO, it can be seen from Table 4 that the absolute value of $E_{O_1-O_2}$ is increased but that of $E_{O_2-H_3}$ is decreased, which is in good agreement with the experimental result (Eq. 2). The decrease in the absolute value of $E_{O_2-H_3}$ is larger in the O_2-coordination (about 1.1 eV) than that in the O_1-coordination (only 0.16 eV), suggesting that reaction (2) proceeds more easily from O_2-

coordination than from O_1-coordination. As described before, O_1-coordination of cobalt(III) is more favorable than O_2-coordination. Therefore, it seems plausible that cobalt(III) forms two complexes with HPO in equilibrium with one another (A and B shown below) and that complex B, though in high concentration, cannot contribute to reaction (2) so much as complex A. That is, the rate of the decomposition of complex B is small compared with that of complex A. In this way, catalytic decomposition of HPO by cobalt(III) will proceed through complexes A and B competitively.



In the case of copper(II), it can be seen from Tables 2 and 3 that the absolute value of $E_{O_2-H_3}$ is decreased by 0.7 eV (O_1-coordination) $\sim$ 1.1 eV (O_2-coordination), which seems to suggest that copper(II) promotes the fission of O_2-H_3 bond of HPO as cobalt(III).* previously, we could not find the evidence for the direct decomposition of HPO by copper(II) proceeding by the fission of O_2-H_3 bond (Eq. 2). However, from the result obtained here, it is expected that copper(II) can promote reaction(2) at the initial stage of the reaction (induction period) where the transformation of copper(II) to active copper(I) occurs. At the later stage of the reaction, rapid oxidation of alkyl radical by copper(II) (Eq. 5) would predominate over reaction 2.

$$R\cdot + Cu^{+2} \longrightarrow R^{+} + Cu^{+1} \qquad (5)$$

* Coordination of copper(II) may accelerate the ionic fission of O-H bond by pyridine (Eq. 6).

$$\overset{\overset{Cu^{+2}}{\downarrow}}{ROOH} + Py \longrightarrow ROO^{-} + H^{+}\cdot Py + Cu^{+2} \qquad (6)$$

However, if reaction (6) occurs, owing to the strong oxidizing ability of ROO^{-}, induced decomposition of HPO to produce alcohol and oxygen[16] or epoxidation of olefine must occur.[17] However, the former was excluded from the results obtained in the previous chapters and the latter was denied from the following fact: That is, when t-butyl HPO was decomposed by copper(II) chloride in the presence of cyclohexene at 40°C in pyridine, cyclohexene oxide could not be obtained.

Summary

MO calculations for the interaction of copper(II) and cobalt(III) with primary and secondary hydroperoxides (HPO) were carried out.

By the coordination of copper(II) to the oxygen atom of HPO, C-H bond of the α-position was found to be weakened, which could explain the effect of copper(II) in the ionic dehydration of HPO by pyridine fairly well.

It was deduced that cobalt(III) coordinated to HPO through its O_1 and O_2 atoms and that the radical decomposition of HPO proceeded from these two species competitively.

The possibility of copper(II) to promote the oxidative fission of the O-H bond of HPO was also suggested.

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Chapter 5 Liquid-phase Oxidation of Cyclohexene Catalyzed by Cu(II)-Cl System

Introduction

It has been well known that the solubility of copper salts is increased by the formation of complexes with alkali chlorides in acetic acid or acetonitrile and these catalyst systems were often used in the chlorination of olefines[1] or in the synthetic reaction of vinyl acetate.[2] Chughtai et al.[3] discussed the structure of copper - chloride ion complex of the type, $CuCl_4^{2-}$, and S.E.Manahan et al. evaluated the stepwise formation constant of the chloro complexes of copper(II) and copper(I) in acetonitrile.[4] Also, similar investigations have been carried out for copper - chloride ion complexes.[5~7]

In this work, we have studied the oxidation of cyclohexene catalyzed by copper(II) chloride - alkali chlorides system and the effect of chloride ion on the catalytic activity of copper(II) was discussed in some detail. Chlorination of olefinic compounds by the catalyst system was also briefly described.

Experimental

Cyclohexene was synthesized by the dehydration of cyclohexanol.[8] The crude cyclohexene was washed with 5% aqueous sodium hydroxide, distilled twice and stored under a nitrogen atmosphere. Cyclohexenyl hydroperoxide was obtained by the autoxidation of cyclohexene. Cyclohexenol was obtained by the reduction of cyclohexenyl hydroperoxide with triphenyl phosphine and cyclohexenone by the decomposition of cyclohexenyl hydroperoxide with copper(II) chloride - pyridine system.* Acetic acid was purified by the usual method. Copper(II) chloride and other reagents (anhydrous, GR grade) were used without further purification.

Oxidation was carried out in a reactor equipped with

an atmospheric pressure gas burette. Fifteen ml of the mixture of cyclohexene and acetic acid containing a catalyst was warmed to the desired temperature (60°C) in a nitrogen atmosphere. Nitrogen was then replaced with oxygen and the reaction started. The decomposition of cyclohexenyl hydroperoxide was carried out in a nitrogen atmosphere and the rate of reaction was followed by iodometric titration of a remaining hydroperoxide.

Analysis of the oxidation products was carried out using a Hitachi gas chromatograph 063 equipped with a flame ionization detector. The column packing was n-decyl phthalate (1m length) and the column temperature was 70 ~ 120°C (5°C/min). Visible spectra were measured by means of a Toshiba-Beckman U.V. spectrophotometer DBG.

Results and Discussion

Catalytic activity of Cu(II) - Cl system The effect of lithium chloride on the catalytic activity of copper(II) chloride was investigated and the results are shown in Fig. 1 and Table 1. In all cases, retardation of the reaction occured after some uptake of oxygen. During the steady state of oxygen absorption, the reacting system was yellowish green or green but a deep blue colour appeared after the retardation. Though the maximum rate of oxygen absorption (Rm) was increased with an increase in the amount of lithium chloride added, a large excess (more than seven parts to one part of copper) resulted in a decrease in the rate. On the other hand, the maximum quantity of oxygen absorbed before the retardation occured was increased linearly with the

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*Cyclohexenone is obtained exclusively in the decomposition of cyclohexenyl hydroperoxide by copper(II) chloride in pyridine; which was reported by S.I.Imamura et al. at the 5th Oxidation Symposium in Osaka. (December 3, 1971)

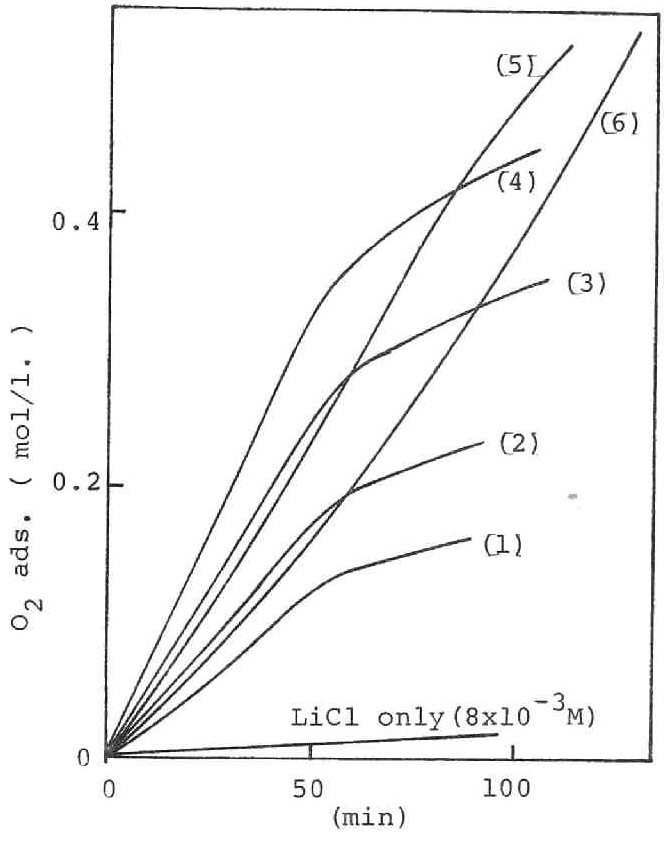

Fig 1. Effect of LiCl on the oxidation of cyclohexe catalyzed by $CuCl_2$

AcOH: 10ml. Cyclohexene: 5ml. $CuCl_2$: $8x10^{-3}$mol/l. $60^{\circ}C$ LiCl($x10^{3}$mol/l.): (1) 0, (2) 8, (3) 24, (4) 48, (5), 80 (6) 200

Table 1 Rm and maxima of absorbed O_2

LiCl ($x10^{3}$M)	Rm ($x10^{3}$M/min)	Max O_2absd (M)
0	3.82	0.136
8	6.82	0.164
24	8.45	0.237
48	10.90	0.306
80	9.13	0.461
200	6.90	0.821

$60^{\circ}C$

AcOH: 10ml

Cyclohexene: 5ml.

$CuCl_2$: $8x10^{-3}$M

increase in the concentration of lithium chloride added. It is clear that lithium chloride increases and maintains the activity of the catalyst. As shown in Fig. 1, lithium chloride without copper salt has little activity.

The effect of various alkali metal chlorides and lithium salts on the catalytic activity of copper(II) chloride were investigated and the results are shown in Table 2. We see that the addition of magnesium chloride, sodium chloride, or potassium chloride increases the maximum quantity of absorbed oxygen and the maximum rate of oxygen absorption (Rm) as in the case of lithium chloride. However, the addition of lithium fluoride, lithium bromide, lithium carbonate,and lithium nitrate has little effect. It has been reported that lithium salts which have a considerable covalent character catalyze the oxidation of hydrocarbon through the activation of a molecular oxygen or through the homolysis of peroxides.[9, 10] However, in our experiment, no such effects could be seen with lithium salts except for lithium chloride. The order of the effect was found to be $KCl > NaCl > LiCl \fallingdotseq MgCl_2$; the greater the ionic character of the added chloride, the more effective for the oxidation. It can, therefore, be said that the effect of the additives on the catalytic activity of copper salt is due to the anionic part, namely, chloride ion, the activity of copper increasing through complex formation with chloride ions.

In Table 3 the activity of various copper compounds - lithium chloride system is shown together with the visible spectra of these system. It can be seen from the table that all copper salts tested are inactive except copper(II) chloride. However, oxidation takes place on addition of lithium chloride to these salts. The visible spectra of the inactive copper salts show absorptions at about 670 nm, while the active catalyst systems containing lithium chloride show absorptions in the wavelength

Table 2. Rm and maxima of absorbed O_2

Additive ($x10^3$M)		Rm ($x10^3$ M/min)	Max. O_2 absd (M)
LiCl	8	6.32	0.161
	24	8.45	0.238
	48	10.90	0.306
$MgCl_2$	8	5.13	0.185
	24	7.68	0.202
	48	8.28	0.328
NaCl	8	6.72	0.196
	24	10.17	0.311
	48	11.37	0.518
KCl	8	9.73	0.184
	24	13.25	0.390
	48	14.00	0.546
LiBr	8	6.22	0.112
	24	6.32	0.131
	48	4.12	0.136
LiF	8	4.82	0.161
	24	5.60	0.109
	48	5.78	0.098
Li_2CO_3	8	6.22	0.136
	24	6.45	0.169
	48	6.03	0.174
$LiNO_3$	8	6.22	0.145
	24	7.98	0.145
	48	8.98	0.147

AcOH: 10ml. Cyclohexene: 5ml.
$CuCl_2$: 8×10^{-3}mol/l. $60^{\circ}C$

longer than 710 nm, which indicates the formation of various types of copper - chloride ion complexes.

The effect of chloride ion on the catalytic activity of transition metals other than copper was also studied. As can be seen from Table 4, lithium chloride has little accelerating effect on the reactions catalyzed by cobalt (II), nickel(II), and manganese(II) chlorides.

The accumulation of cyclohexenyl hydroperoxide (cyclohexenyl HPO) in the reaction was observed at oxygen uptake of 0.136 mol/l and the result is given in Fig. 2.

Table 3 Oxidation activity and λ_{max} of copper salt - LiCl system

Catalyst	Activity	λ_{max}(nm)
$CuCl_2$	○	—
+ LiCl	○	760
$Cu(acac)_2$	X	673
+ LiCl	○	710
CuF_2	X	672
+ LiCl	○	674
$Cu_3(PO_4)_2 3H_2O$	X	—
+ LiCl	○	780
$CuCO_3$	X	—
+ LiCl	○	—
Cu-st*	X	675
+ LiCl	○	770

*st : stearate

Table 4 Oxidation of cyclohexene with MCl_2 - LiCl system

Catalyst	LiCl ($x10^2$M)	Rm ($x10^3$M/min)
$CuCl_2$	0	2.61
	2.4	8.45
$CoCl_2$	0	12.91
	2.4	14.41
$NiCl_2$	0	1.26
	2.4	1.24
$CrCl_2$	0	1.49
	2.4	1.51
$MnCl_2$	0	3.16
	2.4	3.55

AcOH : 10 ml. Cyclohexene : 5 ml.
[Catalyst] : 8×10^{-3}mol/l,

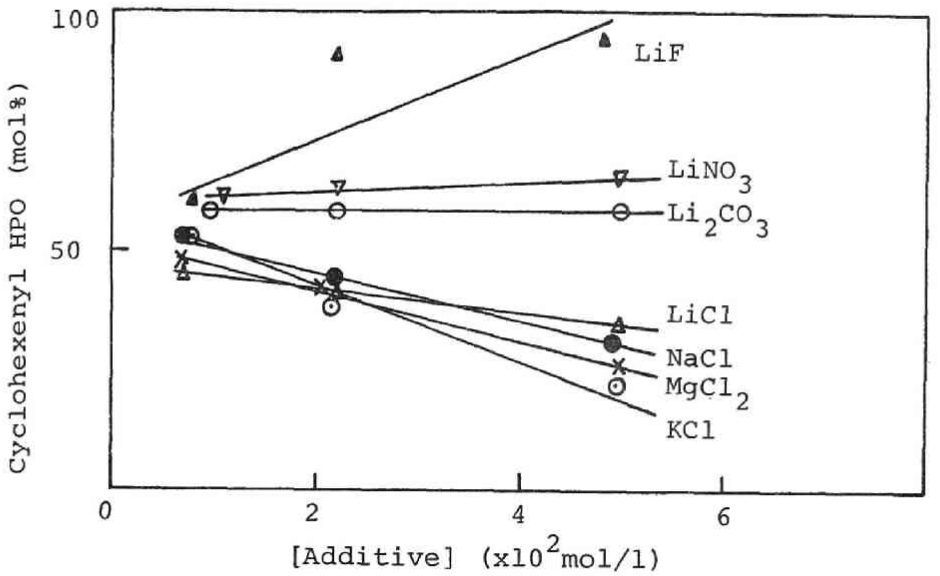

Fig. 2 Effect of additives on cyclohexenyl HPO yield
AcOH: 10 ml. Cyclohexene: 5ml. $CuCl_2$: 8×10^{-3}mol/l. O_2absd.: 0.136 mol/l. 60°C

The addition of lithium carbonate or lithium nitrate has no effect upon the HPO yield, but in the case of various chlorides, the higher the concentration of the chlorides, the lower the yield.

Product distribution The product distribution of the cyclohexene oxidation catalyzed by copper(II) chloride - lithium chloride system was investigated. Main products were cyclohexenyl HPO, cyclohexenol, and cyclohexenone. In addition to these products, two unknown high boiling products, I and II, were detected by gas chromatography. Product I showed an infrared absorption at 1730 cm^{-1} due to carbonyl group and the product II at 3450 cm^{-1} due to hydroxyl group.** It was found that the product II contained chlorine. The relation between the product distribution at the point where the oxygen uptake amounted to 0.136 mol/l and the quantity of lithium chloride added is shown in Fig. 3. We see that as the concentration of lithium chloride is

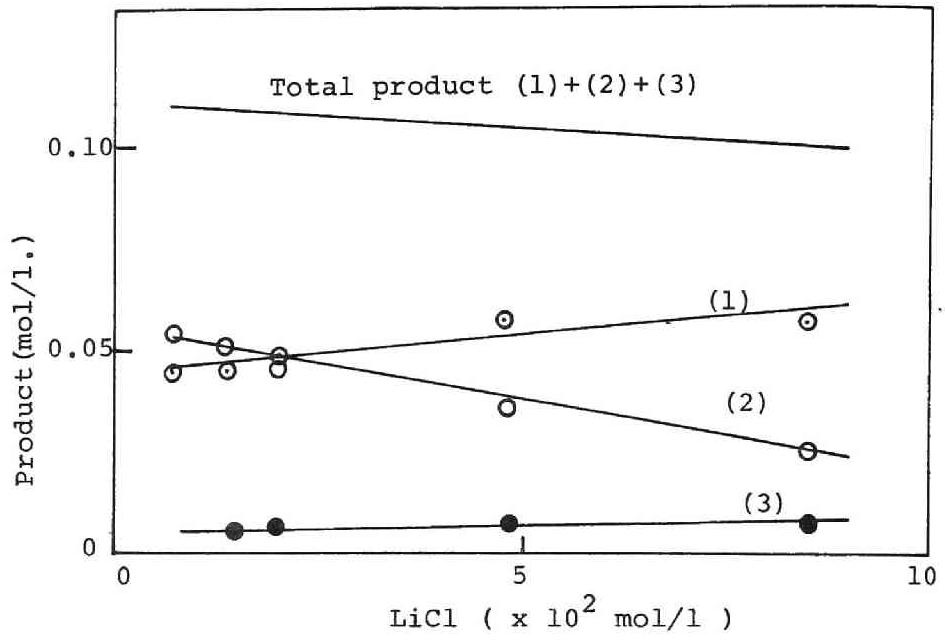

Fig. 3 Effect of LiCl on the product distibution
AcOH : 10ml. Cyclohexene : 5ml. $CuCl_2$: $8x10^{-3}$mol/l. 60°C O_2absd. : 0.136mol/l.
(1) Cyclohexenone (2) Cyclohexenyl HPO
(3) Cyclohexenol

increased, the yield of the HPO decreases and that of cyclohexenone increases. The higher the concentration of lithium chloride, the lower the total yield of these products and, on the contrary, the higher the total yield of the unknown products, which is not shown in the figure. From the result mentioned above, chloride ion seems to be consumed by the chlorination of the reaction products.***

** By the comparison with standard samples, substances I and II proved not to be 3-chlorocyclohexanol or 3-chlorocyclohexenone formed by the chlorination of the conjugated cyclohexenone which is one of the oxidation products..... Moreover, they both did not correspond to 2-chlorocyclohexanone or cyclohexyl acetate.

Decomposition of cyclohexenyl HPO catalyzed by Cu(II) -Cl system It was found that the addition of alkali chlorides decreased the yield of cyclohexenyl HPO, which suggests that chloride ion accelerates the decomposition of the HPO. Therefore, the effect of lithium chloride on the catalytic activity of copper in the decomposition of cyclohexenyl HPO was investigated. As can be seen from Fig. 4, lithium chloride increases the rate of the decomposition remarkably but the decompo-

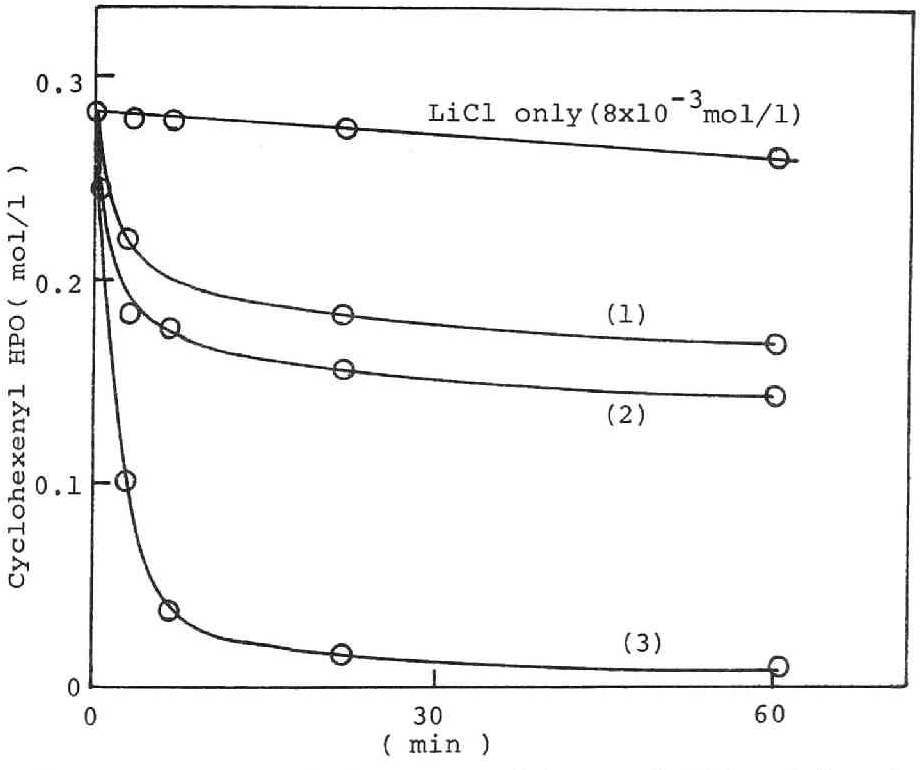

Fig.4 Decomposition of cyclohexenyl HPO catalyzed by $CuCl_2$- LiCl system

AcOH : 10 ml. Cyclohexane : 1o ml. $CuCl_2$: $8x10^{-3}$mol/l. 60°C LiCl (mol/l) (1) 0, (2) $8x10^{-3}$ (3) $8x10^{-2}$

*** After the retardation occured, chloride ion was scarcely detected in the solution with silver nitrate.

sition of the HPO in the presence of lithium chloride alone does not proceed so much. Therefore, the promotion of the catalytic activity by lithium chloride seems to be caused by the complex formation with copper. The decomposition curves resemble that of the oxidation of cyclohexene, that is, retardation occurs after the decomposition of a certain amount of HPO, the colour of the solution turning from yellowish green to deep blue. The quantity of the HPO decomposed by the time the retardation occurred was found to be proportional to the concentration of lithium chloride added. It seems, therefore, that lithium chloride increases the rate of decomposition of HPO and consequently increases that of oxidation.

Change of the catalyst system during the oxidation

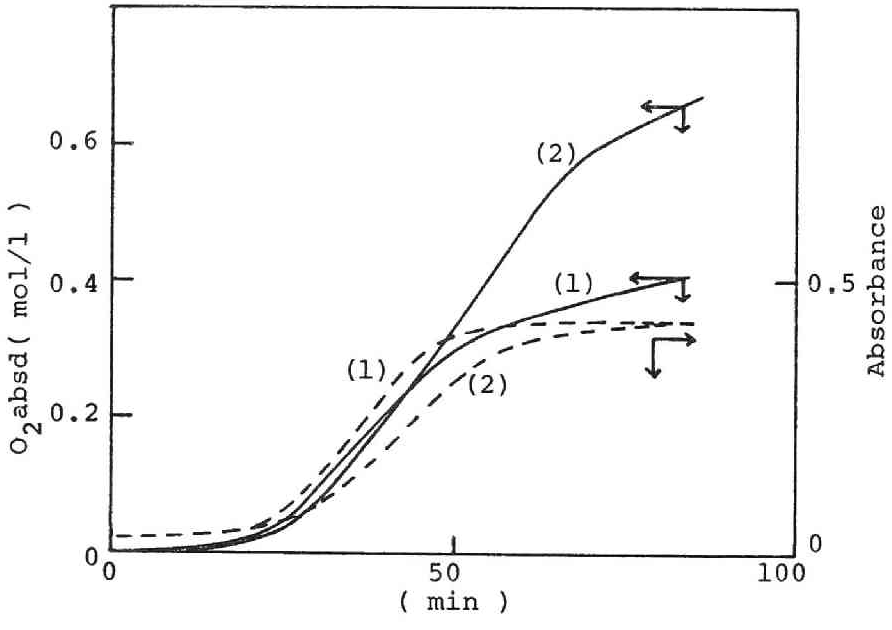

Fig. 5 Time dependence of the visible spectrum
λ_{max} = 680 nm, AcOH: 10ml. Cyclohexene: 5ml. $CuCl_2$: 8×10^{-3}mol/l. 60°C
LiCl(mol/l): (1) 8×10^{-3} (2) 4.8×10^{-2}

In the oxidation of cyclohexene, the colour of the solution changed from yellowish green to green and finally

to deep blue in the course of the reaction, which shows that the condition of the catalyst changed. Therefore, the visible spectra of the reaction system were observed and the effect of lithium chloride upon the change of the state of the catalyst was discussed. It was found that, at the beginning of the reaction, a feeble absorption was observed at 760 nm which seemed to be due to the Cu(II) - Cl complex.[2] Soon after oxidation took place, the absorption disappeared and a new band appeared at 680 nm. From the comparison with the standard reagent, the absorption proved to be due to the copper(II) acetate formed through the ligand exchange of the catalyst with the solvent, acetic acid. The time dependence of the absorption is given in Fig. 5. We see that the absorbance increases during the reaction until the point where the rate of the oxidation begins to decrease and then remains constant. It seems that all the copper changed to copper(II) acetate at the end of the reaction. When the quantity of the lithium chloride was increased, the time was lengthened at which the absorbance became constant [Curve(2) in Fig. 5]. It was found that, at the point where the catalyst became deactivated, addition of more lithium chloride recovered the activity of the system, which shows that the inactive copper(II) acetate was partly changed to the active Cu(II) - Cl complex. It can, therefore, be concluded that lithium chloride contributes to maintain the activity of the catalyst and that the deactivation is caused by the consumption of chloride ion followed by the ligand exchange with acetate anion from solvent forming inactive copper(II) acetate.

Effect of the catalyst concentration Rate dependences of the oxidation on the catalyst concentration are shown in Fig. 6. When the concentration of copper is increased at a constant concentration of lithium chloride, Rm increases but reaches its maximum value at the concen-

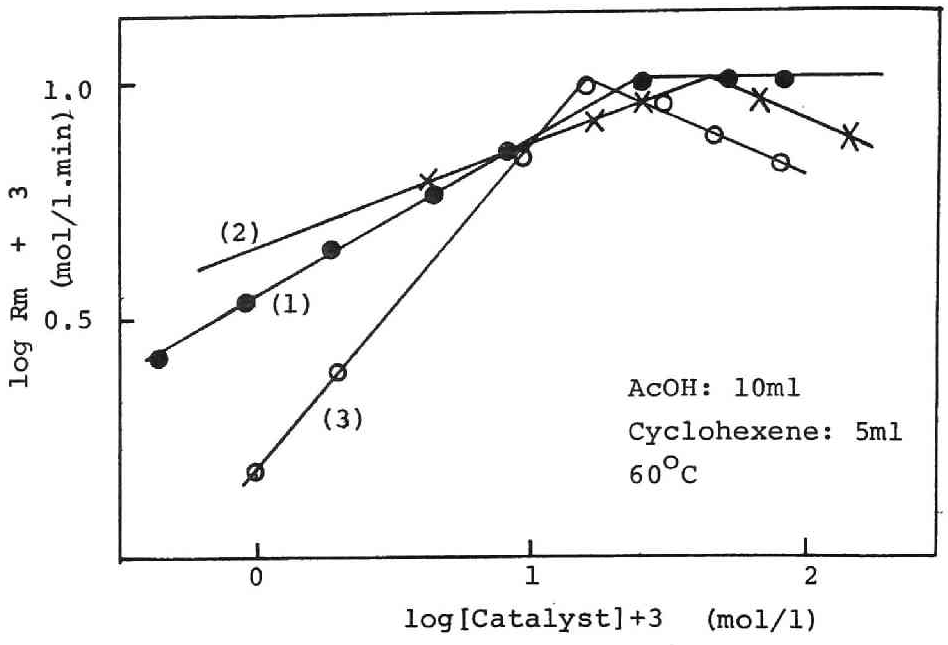

Fig. 6 Rm vs. catalyst concentration
(1) $[CuCl_2]$ dependence, [LiCl] 8×10^{-3} mol/l
(2) [LiCl] dependence, [CuCl] 8×10^{-3} mol/l
(3) $\begin{bmatrix} CuCl_2 & - & LiCl \\ 1 & : & 1 \end{bmatrix}$ dependence

tration of copper about 2.4×10^{-2} mol/l, then remains constant [Curve(1)]. When the concentration of lithium chloride is made to vary at a constant concentration of copper[Curve(2)], Rm reaches the maximum value for a mole ratio of lithium to copper, about 7 : 1, then begins to decrease. The concentration of the Cu(II) - Cl was made to vary at constant lithium to copper concentration of unity. It is shown that Rm also reaches the maximum value at the complex concentration of about 2.0×10^{-2} mol/l and then decreases[Curve(3)]. In all cases the maximum value of Rm is about 1.0×10^{-2} mol/l·min. From curves(2) and (3), it seems that excess lithium chloride retards the reaction. An explanation for the phenomenon may be that excess lithium chloride blocks the active sites of the copper catalyst and prevents hydroperoxide molecules from approaching them. Another explanation may be that, while the active species

is $CuCl_3^-$, excess lithium chloride forms a complex of the type $CuCl_4^{2-}$ which retards the reaction.[11]

Oxidation scheme From the results so far obtained, the oxidation mechanism is schematically drawn as follows.

$$CuCl_2 + Cl \rightleftharpoons CuCl_3^- \ (CuCl_4^{2-}) \quad (1)$$

$$RH \longrightarrow R\cdot \quad (2)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \quad (3)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \quad (4)$$

$$ROOH + CuCl_3^- \ (CuCl_4^{2-}) \longrightarrow ROO\cdot \text{ or } RO\cdot \quad (5)$$

$$CuCl_3^- \ (CuCl_4^{2-}) \xrightarrow[O_2,\ S]{AcOH} Cu(OAc)_2 + \text{Chlorination product} \quad (6)$$

$$Cu(OAc)_2 \xrightarrow{Cl^-} Cu(Cl)(OAc),\ CuCl_2,\ CuCl_3^-,\ CuCl_4^{2-} \quad (7)$$

In reaction (1), copper forms a complex with chloride ion. It seems that the complex is not of a single type but a mixrure of various forms. In reactions (2) ~ (4), cyclohexenyl HPO is formed and the HPO formed is decomposed by the Cu(II) - Cl complex in reaction (5). The increase in the rate of oxidation seems to be due to the high activity of the complex to promote reaction (5). As shown in reaction (6), during oxidation, presumably in the decomposition of the HPO, some ligand exchange occurs through the chlorination of a third body (cyclohexene or its oxidation product), represented by S in reaction (6), and copper(II) acetate is formed causing deactivation of the catalyst system. Addition of alkali metal chlorides to the deactivated system restores the activity of the system. (reaction 7)

In conclusion, it can be said that, in acetic acid, chloride ion increases and maintains the catalytic activity of copper as its ligand.

Summary

Oxidation of cyclohexene catalyzed by Cu(II) - Cl system was carried out in glacial acetic acid. The oxidation of cyclohexene with copper(II) chloride was highly accelerated by addition of various alkali metal chlorides. The decomposition of cyclohexenyl hydroperoxide, an intermediate product of the oxidation, was also accelerated by this catalyst system. Salts other than alkali metal chlorides had little effect. It was concluded that the activation of copper catalyst was due to the chloride ions which form complexes with copper. In the course of the reaction the catalyst system loses its activity through ligand exchange with solvent molecule, acetic acid.

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Appendix

Oxidation of Cyclohexene Catalyzed by Cu(II) - Cl Chloride Ion Transfer

Introduction

Previously we have described that the oxidation of cyclohexene catalyzed by copper(II) chloride was highly accelerated by the addition of various alkali chlorides which formed complex with copper. As the reaction proceeded, it was found that the catalyst deactivated by the consumption of chloride ion. However, we could not elucidate the process of the consumption of chloride ion and identify the chlorinated product.

In this work, we have carried out the oxidation of cyclohexene catalyzed by Cu(II) - Cl system in glacial acetic acid and concerned ourselves mainly with a discussion of the formation of the chlorination product.

Experimental

Material Cyclohexene,[1] cyclohexenol and cyclohexenone were obtained as described previously. Copper(II) acetate anhydride was obtained by the dehydration of copper(II) acetate dihydrate. Lithium chloride was dried at 100°C and stored under a nitrogen atmosphere to avoid moisture. Cyclohexenyl acetate was synthesized from cyclohexenol and acetyl chloride in pyridine[2] and trans-2-chlorocyclohexanol-(1) by the reaction of cyclohexene with hypochloric acid according to the method described by Kendall.[3] Trans-dichlorocyclohexane was obtained by the reaction of cyclohexene with chlorine gas.[4] Other reagents (GR grade) were used without further purification.

Apparatus and procedures Apparatus used and procedures in the oxidation of cyclohexene were the same as described previously. Decomposition of t-butyl hydroperoxide was carried out under a nitrogen atmosphere

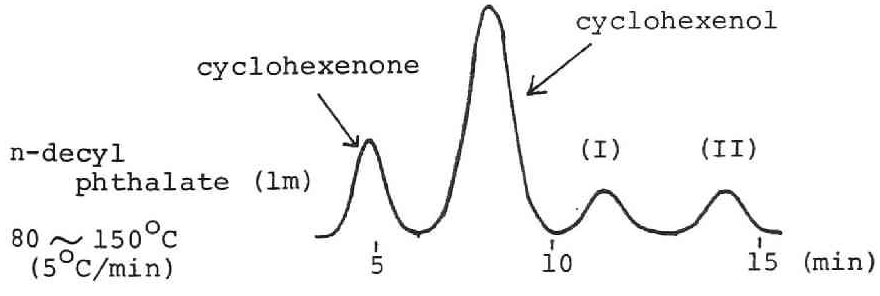
and the reaction was followed by the iodometric titration of a remaining hydroperoxide.

Analytical procedures Identification of products was carried out using a Hitachi Infrared Spectrophotometer 215, a Hitachi Mass Spectrometer RMU-6L and a Hitachi gas chromatograph 063 equipped with a flame ionization detector. Yield of the products were determined by the gas chromatograph using iso-butylphenyl acetate as an internal standard previously calibrated against the authentic sample. The condition for the operation of the gas chromatograph was as follows:

Column ; n-decyl phthalate 1m, Column temperature ; 80 $\sim$ 150°C (3°C/min), Carrier gas ; N_2 30ml/min

Result and Discussion

Identification of the products in the oxidation of cyclohexene catalyzed by Cu(II) - Cl system Oxidation of cyclohexene catalyzed by copper(II) acetate - lithium chloride catalyst was carried out in glacial acetic acid and the reaction products were analyzed by gas chromatograph.* As shown below, two unknown products were observed in addition to cyclohexenol and cyclohexenone. These two unknown products(I) and (II) were collected by gas chromatograph and analyzed by I.R. spectrophotometer



* Cyclohexenyl hydroperoxide was reduced to cyclohexenol by triphenyl phosphine before analysis.

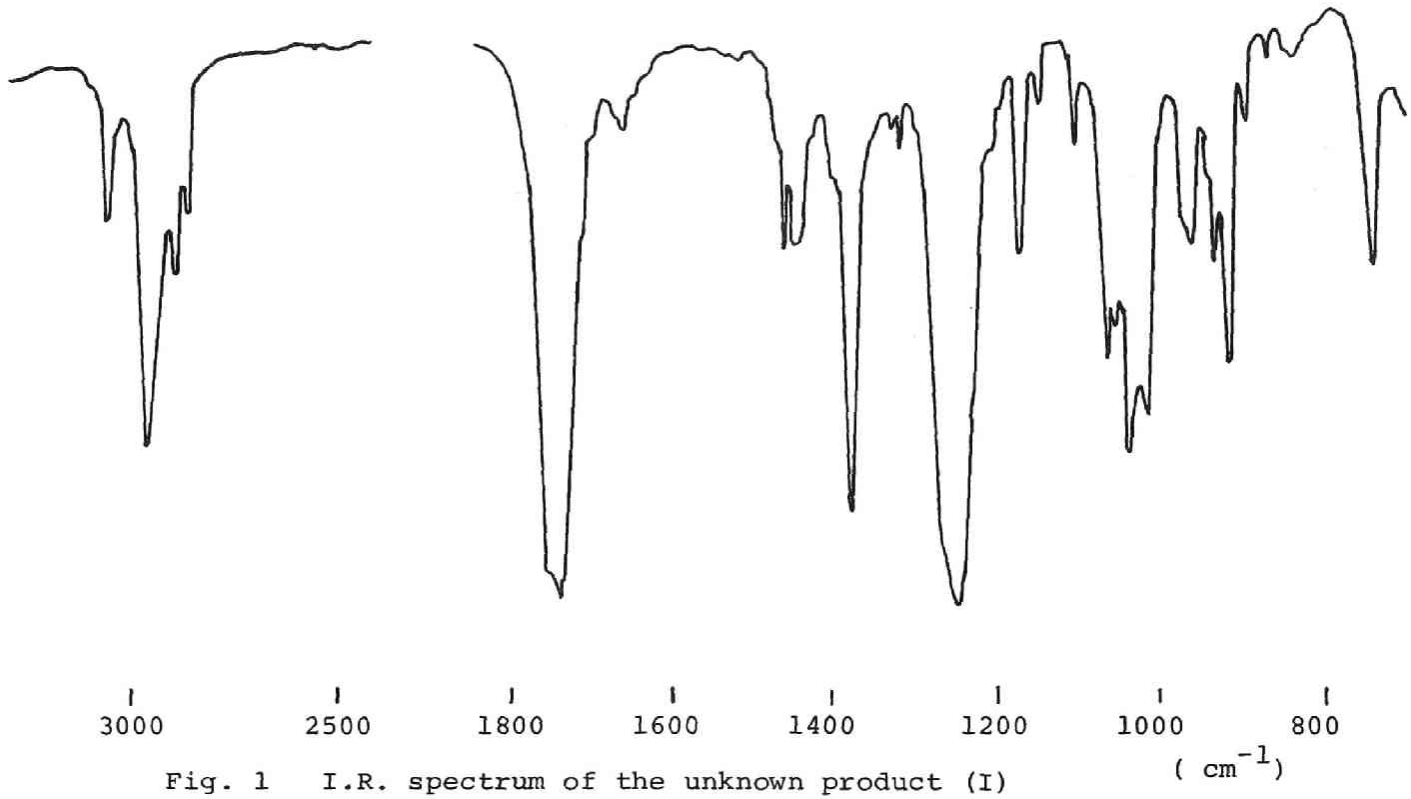


Fig. 1 I.R. spectrum of the unknown product (I)

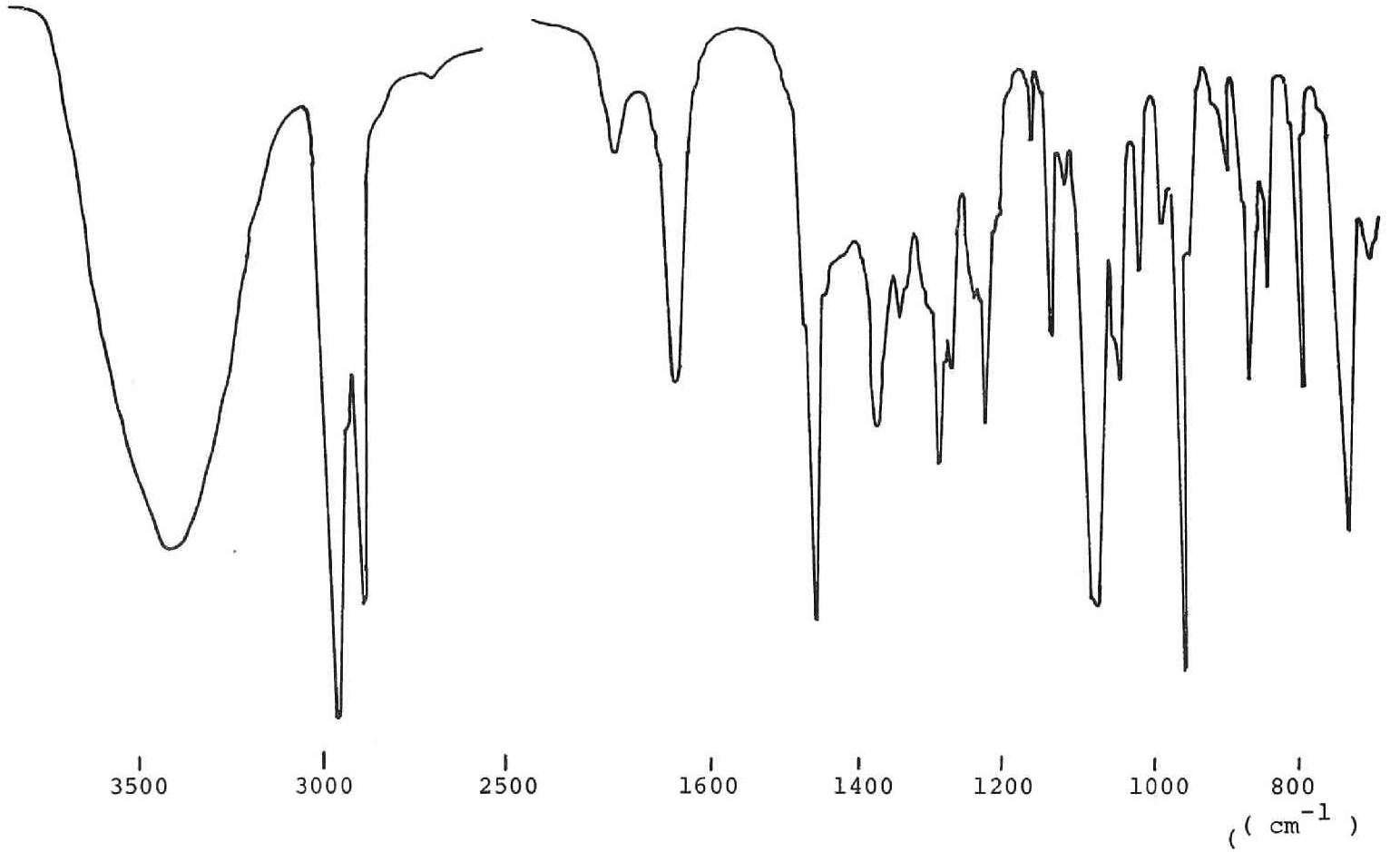
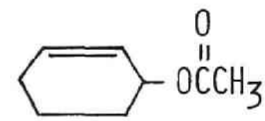


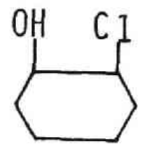
Fig. 2 I.R. spectrum of the unknown compound (II)

and mass spectrometer. I.R. spectra of these two compounds are shown in Figs. 1 and 2. From Fig. 1, it can be seen that the compound (I) shows absorptions at 3040 cm^{-1} (-C=C-), 2960 and 2880 cm^{-1} ($-CH_3$), 2930 and 2860 cm^{-1} ($-CH_2-$), 1740 cm^{-1} (C=O) and 1250 cm^{-1} (ester group). Mass spectrum showed a parent peak at a mass number of 140. From the results obtained, compound (I) seems to be cyclohexenyl acetate and, by the comparison with the standard sample synthesized by a standard method, it proved to be 1-cyclohexenyl acetate.

I.R. spectrum of compound (II) shows an absorptions at 3400 cm^{-1} (-OH), 2950 and 2870 cm^{-1} ($-CH_3$). The absorption at 3040 cm^{-1} due to olefinic bond disappeared. Mass spectrum showed fragments at m/e of 136, 134, 118, 116, 99 etc. The ratio of the intensity of the peak at m/e of 136 and that of 134 was found to be 1 : 3 and, also, the intensity of the peak at m/e of 116 was three times that at 118, which showed that compound (II) containes one chlorine atom. Therefore, it seemed to be chloro-cyclohexanol and, by the comparison with a standard sample, it proved to be trans-2-chloro-cyclohexanol-(1).



M.W. 140



M.W. 134

Accumulation of 1-cyclohexenyl acetate and trans-2-chloro-cyclohexanol-(1) during the reaction Fig. 3 shows the accumulation of these two compounds during the oxidation of cyclohexene. We see that the yields increase as the reaction proceeds but, at the point where

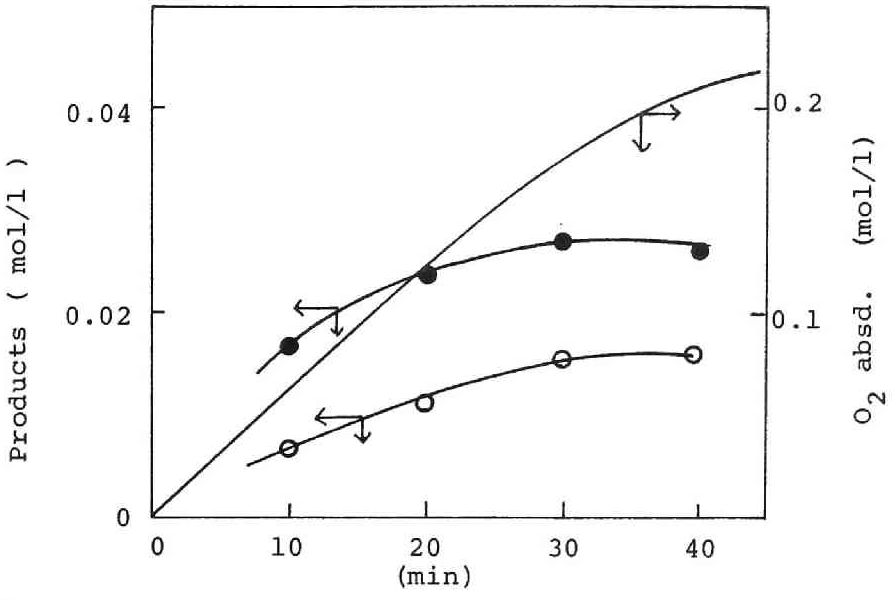


Fig. 3 Accumulation of 1-cyclohexenyl acetate and trans-2-chlorocyclohexanol-(1) during the oxidation of cyclohexene catalyzed by Cu(II)-Cl in acetic acid
[Cyclohexene]: 3.2 mol/l, $[Cu(OAc)_2]$: 8.0×10^{-3}mol/l
[LiCl]: 2.4×10^{-2}mol/l, $60^{\circ}C$
—●— : 1-cyclohexenyl acetate
—○— : trans-2-chlorocyclohexanol-(1)

the rate of the absorption of oxygen begins to decrease, reach maximum values In Fig. 4, the effect of the concentration of lithium chloride on the product yields is shown. The yields were measured at the point where the catalyst deactivated. It can be seen from the figure that the yields of these two compounds increase as the increase of lithium chloride added and that more than 80% of chloride ion is found to be consumed as trans-2-chlorocyclohexanol-(1), which would cause the deactivation of the catalyst system.

It may be considered that 1-cyclohexenyl acetate was formed by the esterification of cyclohexenol which was one of the reaction products with acetic acid. To

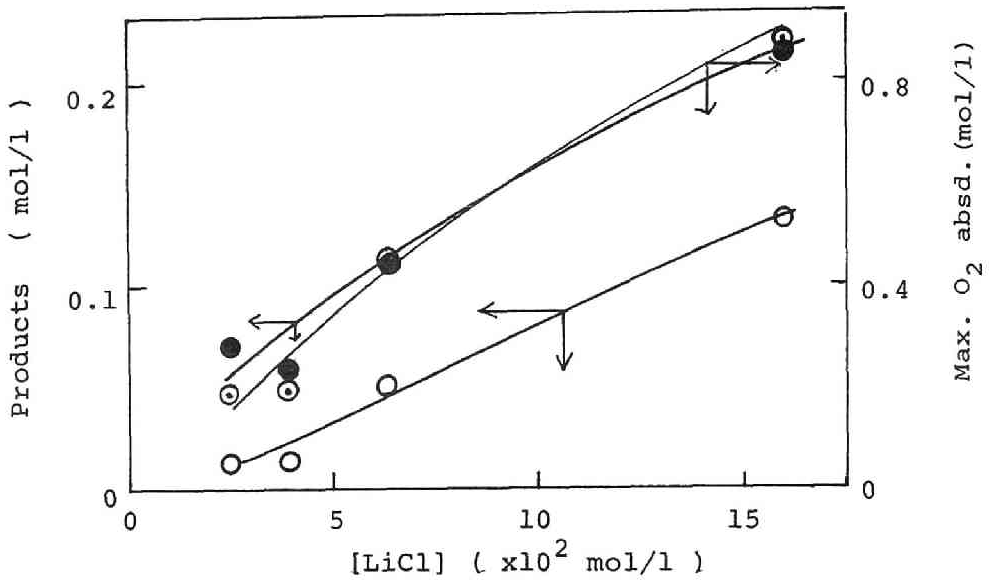


Fig. 4 Accumulation of 1-cyclohexenyl acetate and trans-2-chlorocyclohexanol-(1) after the deactivation of the catalyst

[Cyclohexene]:4.1mol/l, [$Cu(OAc)_2$]:8.0x10^{-3}mol/l

Solvent : AcOH, 60°C

—●— 1-cyclohexenyl acetate

—○— trans-2-chlorocyclohexanol-(1)

—⊙— maxima of O_2 absorbed

clarify this, cyclohexenol was refluxed at the reaction temperature (60°C) in acetic acid and the result is shown in Fig. 5. From the figure, we see that the yield of 1-cyclohexenyl acetate is almost constant throughout the reaction, which seems to suggest that 1-cyclohexenyl acetate is formed not during the oxidation at 60°C but during the analytical procedure in the column or injector of the gas chromatograph. However, with respect to this, more detailed experiment is necessary.

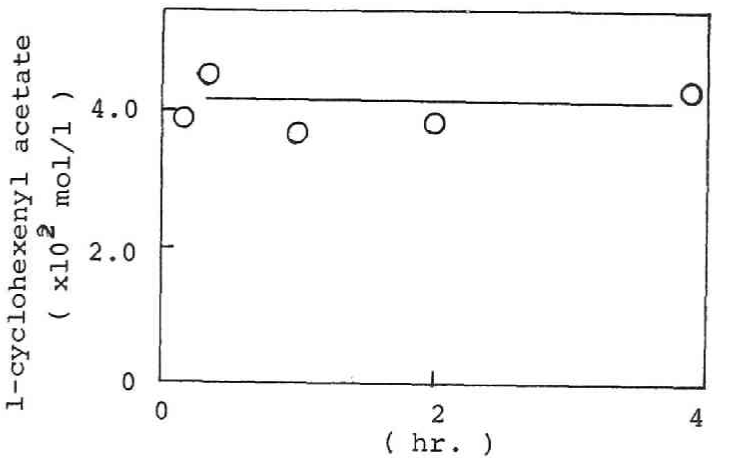


Fig. 5 Accumulation of 1-cyclohexenyl acetate by the reaction of cyclohexenol with acetic acid at 60°C
AcOH : 40 ml, [Cyclohexenol]: 0.255mol/l

Decomposition of t-butyl hydroperoxide catalyzed by Cu(II) - Cl system in the presence of cyclohexene

As stated earlier, Cu(II) - Cl system exhibited high activity to decompose cyclohexenyl hydroperoxide but, during the decomposition, the catalyst lost its activity by the consumption of chloride ion. This suggests that Cu(II) - Cl complex easily loses chloride ion in the presence of hydroperoxide. To clarify the chloride ion transfer of Cu(II) -Cl system to olefinic compound, the decomposition of t-butyl hydroperoxide catalyzed by this system was carried out in acetic acid - cyclohexene mixed solvent. The analysis of the reaction products after the completion of the decomposition showed the formation of two unknown substances in addition to the decomposition products of t-butyl hydroperoxide. By the same procedure mentioned previously, these were identified as 1-cyclohexenyl acetate and trans-dichloro-cyclohexane respectively. The yields of trans-dichloro-cyclohexane at the reaction temperature of 60°C and 100°C

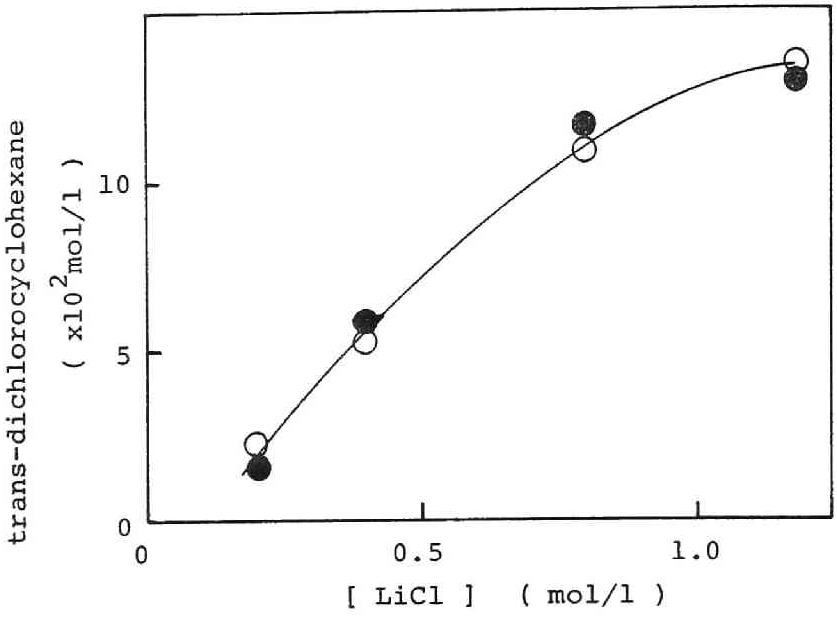


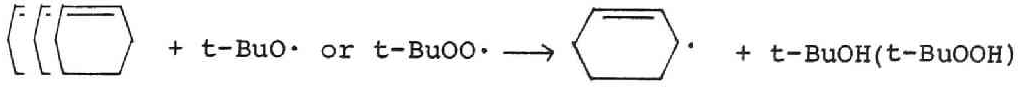
Fig. 6 Accumulation of trans-dichlorocyclohexane in the decomposition of t-butyl hydroperoxide catalyzed by Cu(II)-Cl system
AcOH : 20 ml, [Cyclohexene]: 2.0 mol/l
[t-Butyl hydroperoxide]: 0.281 mol/l, [$Cu(OAc)_2$]: $4.0x10^{-2}$mol/l
60°C
100°C

were plotted against the concentration of lithium chloride added and the result is shown in Fig. 6. We see that the yield of trans-dichlorocyclohexane increases as the increase of lithium chloride and that about 30% of chloride ion added is consumed by the chlorination of cyclohexene. Though it has been reported that chlorination of olefine by Cu(II) - Cl system does not proceed at such a low temperature as 60°C[5], from our result, chloride ion transfer seems to occur easily in the presence of hydroperoxide. In the oxidation of cyclohexene, trans-2-chlorocyclohexanol was obtained as a chlorinated product and its yield (80%) was higher than that of trans-dichlorocyclohexane (about 30%). Therefore, it

appears that trans-2-chlorocyclohexanol is formed by the chlorination of cyclohexenol or cyclohexenone which are the products in the oxidation of cyclohexene and that these oxidation products are more easily chlorinated than cyclohexene.

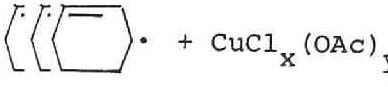
In the case of the decomposition of t-butyl hydroperoxide where cyclohexenol is not present, 1-cyclohexenyl acetate is also obtained (yield of about 14% based on cyclohexene added). This may be that the ligand transfer of acetate anion to cyclohexenyl radical occurs as shown below.

$$\text{t-BuOOH} \xrightarrow{CuCl_x(OAc)_y} \text{t-BuO}\cdot \text{ or t-BuOO}\cdot$$

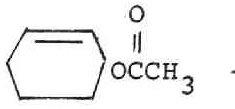


$$+ \text{ t-BuO}\cdot \text{ or t-BuOO}\cdot \longrightarrow$$

$$+ \text{ t-BuOH(t-BuOOH)}$$



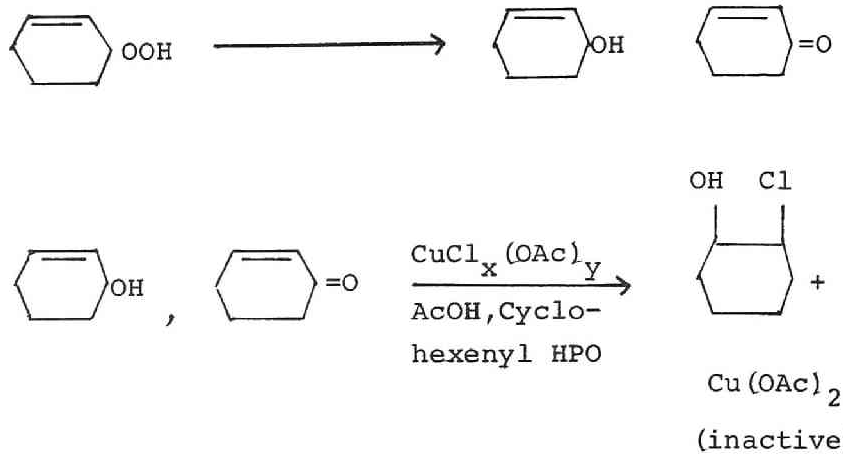
$$+ CuCl_x(OAc)_y \longrightarrow$$



$$+ CuCl_x(OAc)_{y-1}$$

However, as it is reported that the ligand transfer of copper salt to alkyl radical did not occur when acetate anion coordinated to copper as a ligand, more detailed experiment is necessary with respect to this.

In conclusion, the consumption of chloride ion during the oxidation of cyclohexene is considered as follows: That is, during the reaction, Cu(II) - Cl system transfers chloride ion to cyclohexenol or cyclohexenone which are the products of the decomposition of cyclohexenyl hydroperoxide. This step is considered to be accelerated by the reaction of copper with cyclohexenyl hydroperoxide. Then acetate anion from solvent enters into the ligand site of copper and forms copper(II) acetate, which would cause the deactivation of the catalyst system.



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Chapter 6 Oxidation of 1,2,3,4-Tetrahydronaphthalene Catalyzed by Cu(II) - Cl System

Introduction

Previously we have carried out the oxidation of cyclohexene catalyzed by Cu(II) - Cl system[1~6] and described that the activity of copper(II) was highly increased by the complex formation with chloride ion. During the reaction, chloride ion was consumed by the chlorination of the olefinic bond of cyclohexene or its derivatives and the catalyst was found to be deactivated. Owing to the rapid deactivation of the catalyst, the kinetics of the reaction could not be discussed.

In this chapter, we have studied the oxidation of 1,2,3,4-tetrahydronaphthalene (tetralin) to clarify the kinetic behaviour of the Cu(II) - Cl system and elucidated the effect of chloride ion in some detail.

Experimental

Material Commercial tetralin was washed with 5% aqueous sodium hydroxide and concentrated sulfuric acid, distilled twice under reduced pressure and stored under a nitrogen atmosphere. 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide (THPO) was obtained by the autoxidation of tetralin and recrystallized twice from petroleum ether. Acetic acid was purified by the standard method. Anhydrous copper(II) acetate was obtained by the dehydration of copper(II) acetate dihydrate. Lithium chloride was dried at 100°C and then stored under a nitrogen atmosphere. Other reagents (GR grade) were used without further purification.

Apparatus and procedures The oxidation procedures and the apparatus were the same as described in the previous chapter.

Analytical procedures THPO was analyzed by an iodometric titration and other oxidation products by the

use of a Hitach gas chromatograph 063 equipped with a flame ionization detector. The column packing was PEG 1000 (lm) and the column temperature was maintained at 150°C. Visible spectra were measured by means of a Toshiba-Beckman U.V. spectrophotometer DBG. The apparatus used in the ESR experiment was the JES-PE type of Japan Electron Optics Laboratory. Spectra were measured at 100°C ~ -40°C and the temperature was maintained by passing cooled nitrogen gas or hot air through the low-temperature cavity. Determination of g-value was carried out by the use of Mn^{+2} marker as a standard.

Result and Discussion

Visible spectra of the Cu(II) - Cl complex in glacial acetic acid Visible spectra of the Cu(II) - Cl complex in glacial acetic acid were observed at various ratio of lithium chloride to copper(II) acetate concentration and the result is shown in Table 1. Copper(II)

Table 1 Visible spectra of $Cu(OAc)_2$ - LiCl

Solvent : AcOH
Measured at room temperature

$LiCl/Cu(OAc)_2$	1	2	3	4	5	6	10
λ_{max} (nm)	680	690	700	710	750	800	>800

acetate without lithiun chloride showed an absorption at 680 nm. By the addition of lithium chloride, more than one part to one part of copper, this absorption disappears and a new absorption appeares, As the concentration of lithium chloride is increased, the new absorptions shift to higher wave-length region, that is, the colour of the solution changes from blue to green and finally to yellow, which suggests that acetate anion undergoes

ligand exchange with chloride ion and complexes which have copper - chloride ion bonds are formed as shown below:[1)]

$$Cu(OAc)_2 \overset{Cl^-}{\rightleftharpoons} CuCl(OAc) \overset{Cl^-}{\rightleftharpoons} CuCl_2 \overset{Cl^-}{\rightleftharpoons} CuCl_3^- \overset{Cl^-}{\rightleftharpoons} CuCl_4^{2-}$$

Oxidation of tetralin catalyzed by Cu(II) - Cl

In Fig. 1, oxidation curves are shown. We see that lithium chloride accelerates the reaction. Copper(II) acetate without lithium chloride was found to be inactive for the oxidation. In Fig. 2, the maximum rate of

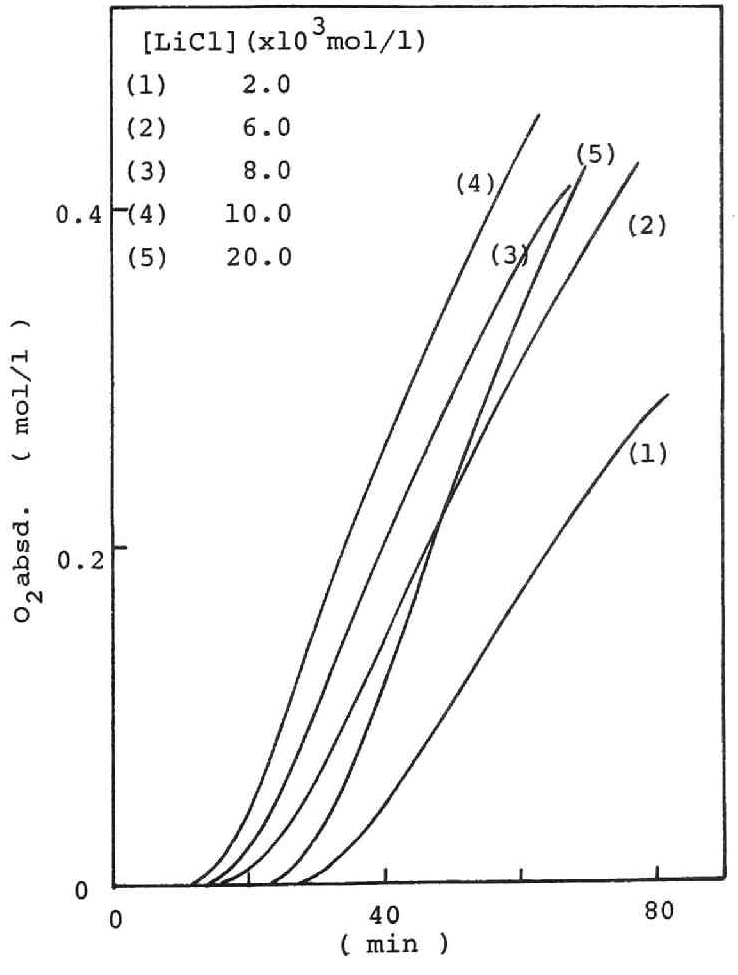

Fig. 1 Oxidation of tetralin catalyzed by Cu(II) - Cl

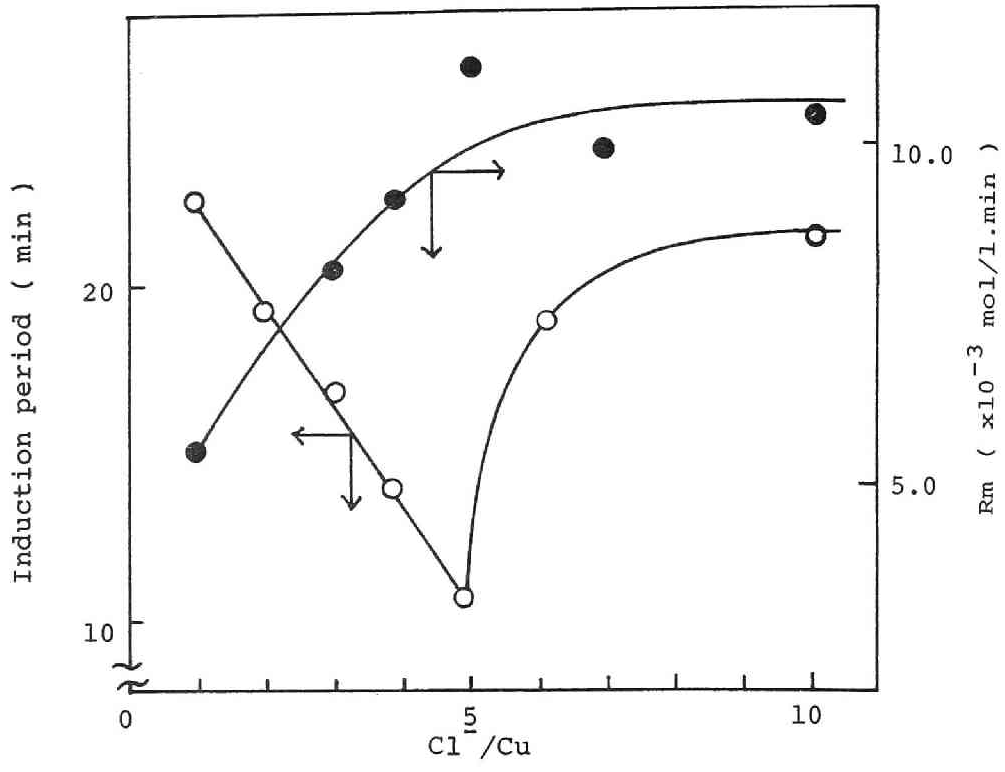

Fig. 2 Effect of LiCl concentration on Rm and induction period
$Cu(OAc)_2$: 2.0×10^{-3} mol/l Tetralin : 1.25mol/l Solvent : AcOH $80^{\circ}C$

oxidation (Rm) and the induction period are plotted against the mole ratio of lithium chloride to copper(II) acetate at constant concentration of copper. We see that, as the concentration of lithium chloride increases, Rm increases and reaches maximum value at the mole ratio of five and hereafter becomes constant. The induction period also takes minimum value at this mole ratio and is rather prolonged hereafter. From these results, it seems that apparently most active species is formed at the chloride ion to copper mole ratio of five. Rather retarding effect of excess lithium chloride will be discussed later.

Consumption of chloride ion during the reaction

It was found that, during the oxidation, the colour of

Table 2 Time dependence of visible spectrum in the oxidation of tetralin

Reaction Time (min)	λ_{max} (nm)
0	750
15	740
20	710
30	690
40	680
55	680
115	680
180	680

Solvent:AcOH LiCl: 1.0×10^{-2}M
$Cu(OAc)_2$: 2.0×10^{-3}M, at room temp.

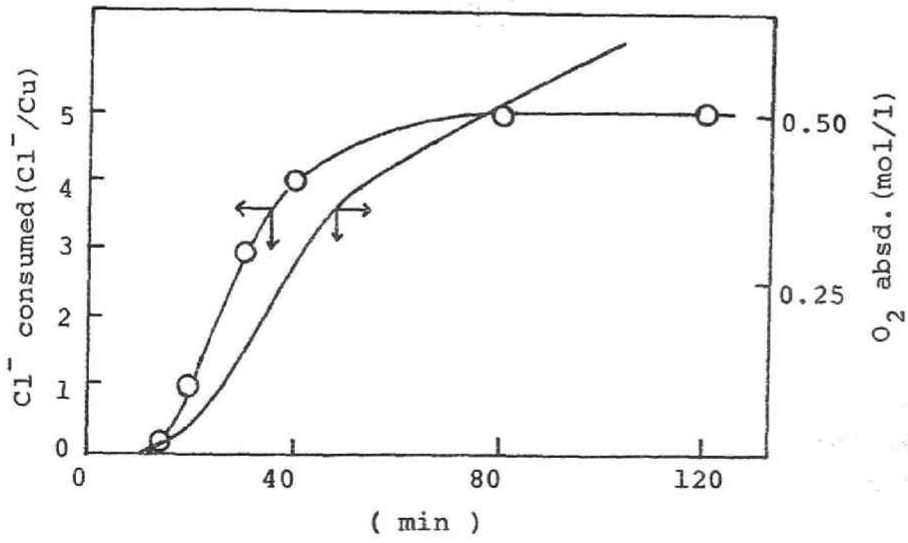

Fig. 3 Consumption of Cl^- during the reaction
$Cu(OAc)_2$: 2.0×10^{-3}mol/l LiCl : 1.0×10^{-2}mol/l Tetralin : 1.25mol/l
Solvent : AcOH $80^{\circ}C$

the solution changed from yellow to green and finally to blue, which shows that the state of the catalyst gradually changes. Therefore, the visible spectra of the solution were observed and the result is listed in Table 2. The catalyst system used was of the composition, Cu : Cl = 1 : 5. It can be seen from Table 2 that the absorption by the catalyst system gradually shifts to lower wavelength region as the reaction proceeds. After fourty minutes, the absorption at 680 nm, due to copper(II) acetate, appears. The absorbance after 111 minutes, which is not shown in the table, indicated that all the copper turned to copper(II) acetate at this point. From these results, it seems that the chloride ion is consumed during the reaction and changed to inactive forms which cannot coordinate to copper. The quantity of consumed chloride ion is estimated from Table 1 and Table 2 and plotted against the reaction time as shown in Fig. 3. We see that the consumption of chloride ion occurs as soon as the induction period is over.*

Oxidation by the catalyst system, Cu : Cl = 1 : 5

The oxidation of tetralin was carried out using the most active catalyst system with the composition of chloride ion to copper mole ratio of five. The rate dependences on catalyst, tetralin and oxygen concentrations are shown in Fig. 4. It can be seen from the figure that the rate is proportional to $[\text{Catatalyst}]^{1/2}$ and $[\text{Tetralin}]^{3/2}$ and is independent of the oxygen concentration near 1 atm. Therefore, the overall rate expression was obtained as follows, where RH represents tetralin.

$$-dO_2/dt = k\,[\text{Catalyst}]^{1/2}[\text{RH}]^{3/2}[O_2]^0 \qquad (1)$$

The apparent activation energy was found to be 17.0Kcal/mol.

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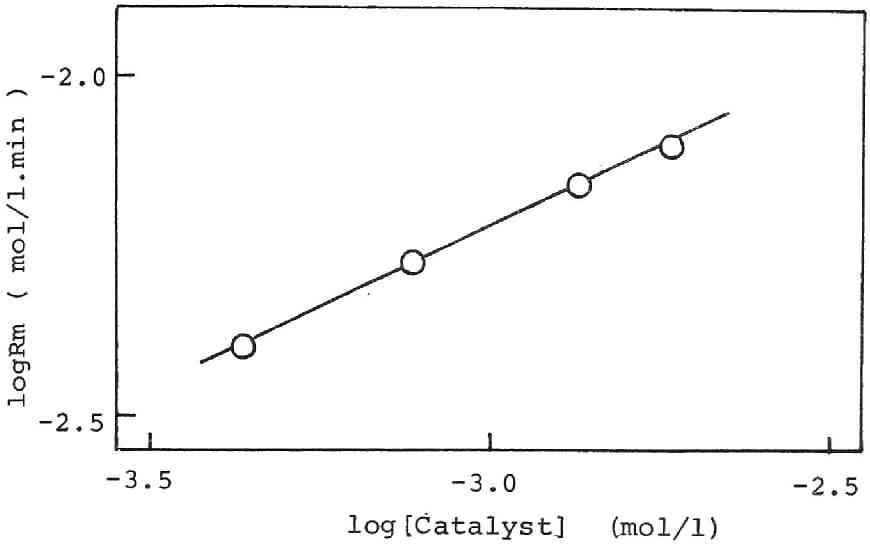
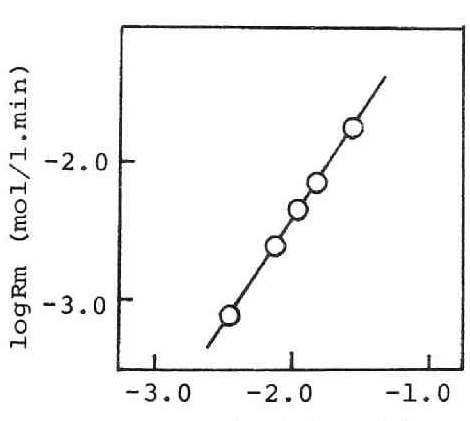
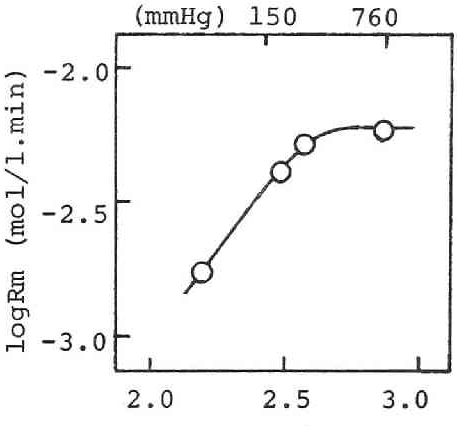
* Chlorination products were not analyzed.





$Cu(OAc)_2$: 2.0×10^{-3} mol/l
LiCl : 1.0×10^{-2} mol/l



$Cu(OAc)_2$: 2.0×10^{-3} mol/l
LiCl : 1.0×10^{-2} mol/l

Fig.4 Rate dependences on the reactants

$Cu : Cl^- = 1 : 5$
Solvent : AcOH
$80^{\circ}C$

However, we cannot discuss the mechanism of the reaction from Eq. (1) because, in the procedure employed to obtain Eq.(1), the rates were calculated from the maximum slope of the oxidation curves and, as stated earlier, the state of the catalyst did not remain constant during the reaction owing to the consumption of chloride ion.

Product distribution In Fig. 5, the product distribution in the oxidation of tetralin is shown. Main products were 3,4-dihydro-1(2H)naphthalenone (α-tetralone), 1,2,3,4-tetrahydro-β-naphthol (α-tetralol) and THPO. As shown in the figure, the yield of THPO is considerably low and there is no steady state concentration. Tobolsky[7] reported that the maximum rate of

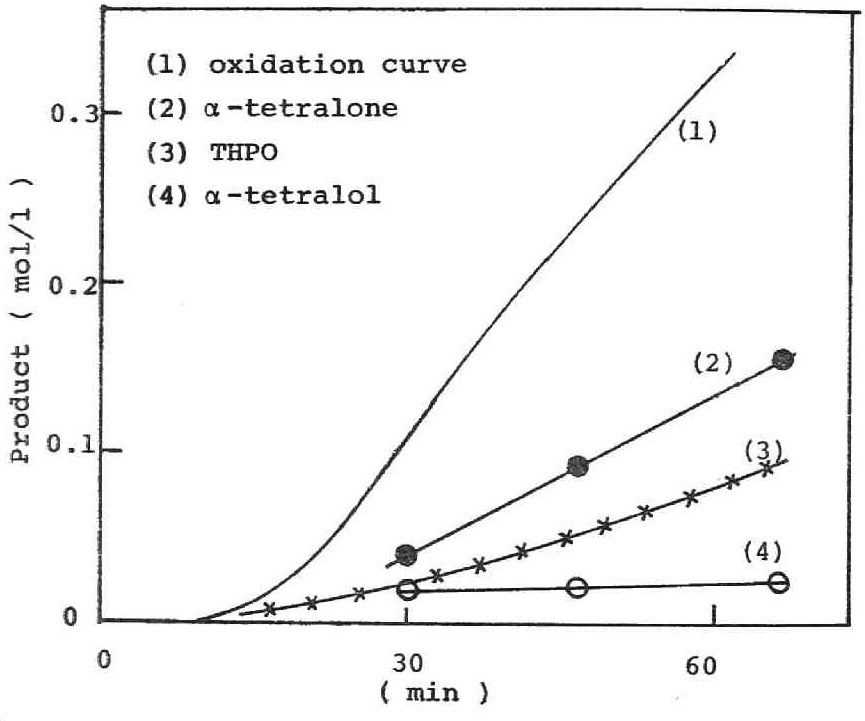


Fig. 5 Product distribution in the oxidation of tetralin

$Cu(OAc)_2$: 2.0×10^{-3} mol/l
LiCl : 1.0×10^{-2} mol/l Solvent : AcOH $80^{\circ}C$

oxidation was proportional to $[RH]^2$ where the steady state concentration of hydroperoxide was obtained. On the other hand, the rate is proportional to $[RH]^1$ where the amount of absorbed oxygen is almost equal to the amount of hydroperoxide formed. Our result would be the intermediate case between these two extreme, so it seemed that the one half order dependence on hydrocarbon concentration was obtained. (Eq. 1)

Decomposition of THPO catalyzed by Cu(II) - Cl system

Catalytic activity of Cu(II) - Cl in the decomposition of THPO was investigated. Copper(II) acetate was found to be inactive, but, on addition of lithium chloride, reaction proceeded without any induction period.** In Table 3, the effect of lithium chloride at the constant concentration of copper is shown. We see that the initial rate of decomposition is increased with the increase of lithium chloride added and takes maximum value at the lithium chloride to copper mole ratio of five and hereafter becomes almost constant. This phenomenon

Table 3 Decomposition of THPO catalyzed by Cu(II) - Cl

$LiCl/Cu(OAc)_2$	Initial rate (mol/l.min)	THPO decompd. (mol/l)
1	4.00×10^{-3}	0.085
3	9.70×10^{-3}	0.113
5	1.68×10^{-2}	0.132
7	1.53×10^{-2}	0.145
10	1.55×10^{-2}	0.149

Solvent : AcOH $50^{\circ}C$ THPO : 0.165mol/l
$Cu(OAc)_2$: 2.0×10^{-3}mol/l

**Lithium chloride alone also had no catalytic activity.

resembles to that observed in the oxidation of tetralin and, from this, it may be deduced that the high catalytic activity of Cu(II) - Cl system in the oxidation is attributable to its ability to decompose THPO. In the decomposition products, oxygen could not be detected. This shows that the reaction (2) does not play an important role in the decomposition.

$$ROOH + Cu^{+2} \longrightarrow ROO\cdot + H^{+} + Cu^{+1} \qquad (2)$$

$$(2ROO\cdot \longrightarrow RO\cdot + O_2)$$

From the initial rate of the decomposition, the overall rate expression was obtained as follows:***

$$-d[THPO]/dt = k[THPO]^{1.0}[Catalyst]^{1.0} \qquad (3)$$

Oxidation initiated by THPO - Cu(II)-Cl system

In the previous section, it was deduced that the catalytic activity of Cu(II)-Cl to initiate the oxidation was due to its ability to decompose THPO. Therefore, the decomposition of THPO by Cu(II)-Cl is expected to be the main initiating process in the oxidation. In order to confirm this, a series of oxidation experiments has been carried out; that is, a known amount of THPO was added at the beginning of the reaction and the rate dependences on the concentration of THPO, catalyst and tetralin were observed. The catalyst system, Cu : Cl = 1 : 10, was used as in the case of the decomposition of THPO. Fig. 6 shows the rate dependence on the catalyst concentration. We see that the reaction proceeds without any induction period and that the initial rate

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***The catalyst system, Cu : Cl = 1 : 10, not the most active one, Cu : Cl = 1 : 5, was rather employed to minimize the change of the condition of catalyst during the initial stage of the reaction.

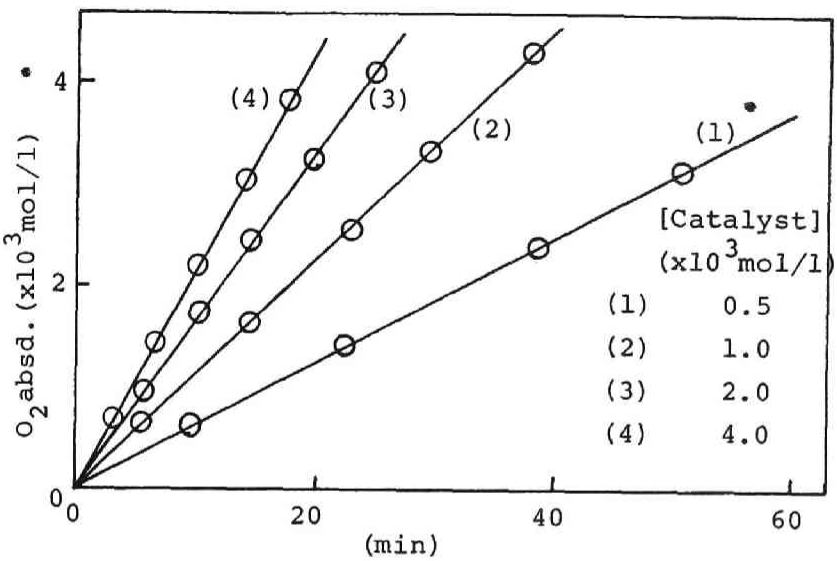


Fig. 6 Oxidation of tetralin initiated by Cu(II)-Cl - THPO system
Tetralin:1.25mol/l THPO:0.1mol/l
Solvent:AcOH Cl^-/Cu = 10 35°C

corresponds to the maximum one, which enables us to discuss the kinetics by the initial rate. The rate dependences on the concentrations of tetralin and THPO are also given in Fig. 7. From Figs. 6 and 7, the overall rate expression for the decomposition of THPO was obtained as follows, where RH represents tetralin.

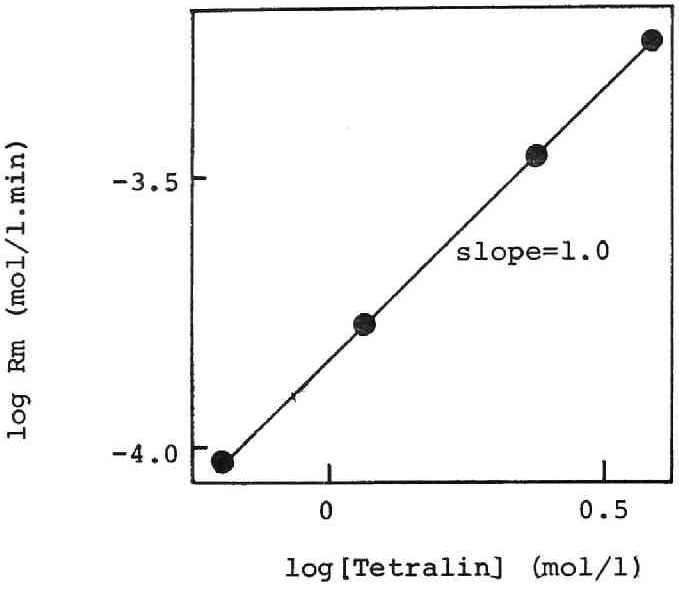
$$-d[O_2]/dt = k[\text{Catalyst}]^{0.55}[RH]^{1.0}[\text{THPO}]^{0.72} \qquad (4)$$

Oxidation mechanism From the results obtained above, the mechanism of the oxidation is given as follows, where the initiating process is the decomposition of THPO (Eq. 5).

$$\text{THPO} + [\text{Catalyst}] \xrightarrow{k_1} \text{radical} \xrightarrow{RH} R\cdot \qquad (5)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \qquad (6)$$

$$RO_2\cdot + RH \xrightarrow{k_3} ROOH + R\cdot \qquad (7)$$



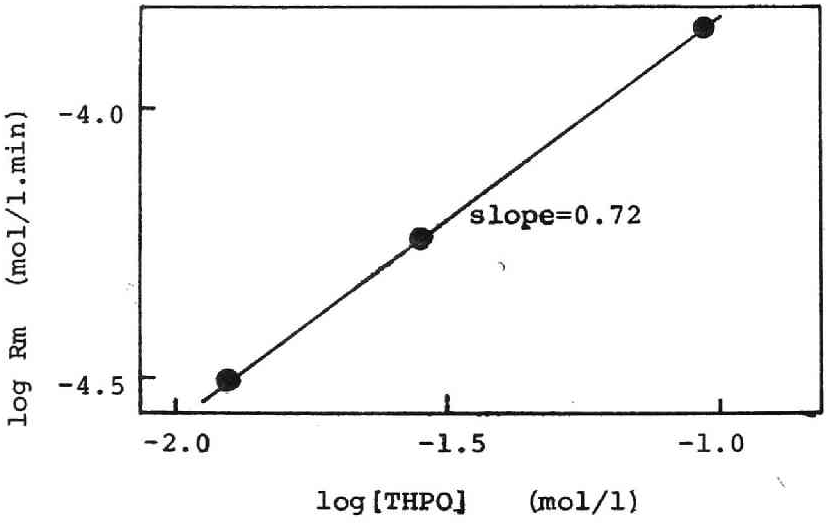


Fig. 7 Oxidation of tetralin initiated by Cu(II)-Cl - TPHO system

$Cu(OAc)_2$: 2.0×10^{-3}mol/l LiCl : 2.0×10^{-2}mol/l
Tetralin : 1.25mol/l Solvent : AcOH $35^{\circ}C$

$$RO_2\cdot + RO_2\cdot \xrightarrow{k_6} \text{inactive product} + O_2 \quad (8)$$

From Equation (5) and Equation (8),

$$-dO_2/dt = k_3\sqrt{Ri/k_6}[\ RH\ ] \quad (9)$$

where

$$R_i = k_1[\ \text{Catalyst}\ ]^{1.0}[\ \text{THPO}\ ]^{1.0} \quad (3)$$

then

$$-dO_2/dt = k_3\sqrt{k_1/k_6}[\ \text{Catalyst}\ ]^{1/2}[\ \text{THPO}\ ]^{1/2}[\ RH\ ]^{1.0} \quad \cdots\cdots \quad (10)$$

where RH is tetralin. The rate expression (Eq. 10) agrees with the observed one (Eq. 4) considerably well with the exception concerning the THPO dependence. This discrepancy in respect to the THPO concentration can not be explained now.

ESR spectra of the catalyst system To clarify the form of Cu(II) - Cl complex and the accelerating effect of chloride ion, ESR spectra of the catalyst system were observed. Copper(II) ion has nine electrons in its 3d-orbitals, so ESR signal must be observed. However, as shown in Fig. 8, copper(II) acetate in glacial acetic acid shows no signal; which can be explained by the following fact. That is, copper(II) acetate has a dimer structure and the distance between each copper atoms is only 2.64 Å, so there is extensive quenching of the spin moment of copper(II) ion.[8] (see Fig. 9) When lithium chloride is added to the system, an asymmetric signal begins to appear, which suggests that the copper(II) acetate dimer is decomposed to monomer species. In Fig. 10, the intensity of the signal (relative to the intensity of Mn^{+2} marker) is plotted against the quantity of lithium chloride added. It is seen that the intensity, that is, the concentration of monomer species takes a maximum value at the chloride ion to copper mole ratio

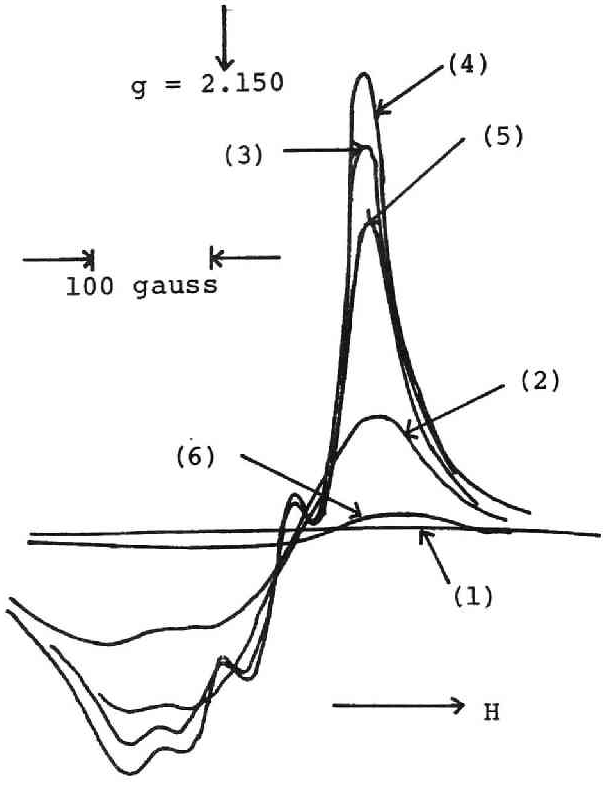


Fig. 8 ESR spectra of Cu(II)-Cl complex

$Cu(OAc)_2$: 2.80×10^{-3} mol/l

Solvent : AcOH

Measured at room temperature

	Cl^-/Cu
(1)	0
(2)	1
(3)	3
(4)	5
(5)	10
(6)	200

near five. As described previously, in the oxidation of tetralin or in the decomposition of THPO, the most active catalyst system was found to be of the composition, Cu : Cl = 1 : 5. The phenomenon shown in Fig. 10 seems to explain these results fairly well; that is, one of the accelerating effect of chloride ion is to decompose the

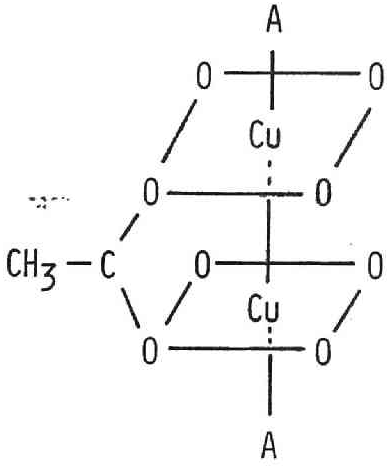


Fig. 9 Structure of copper(II) acetate
Only one bridging group is shown

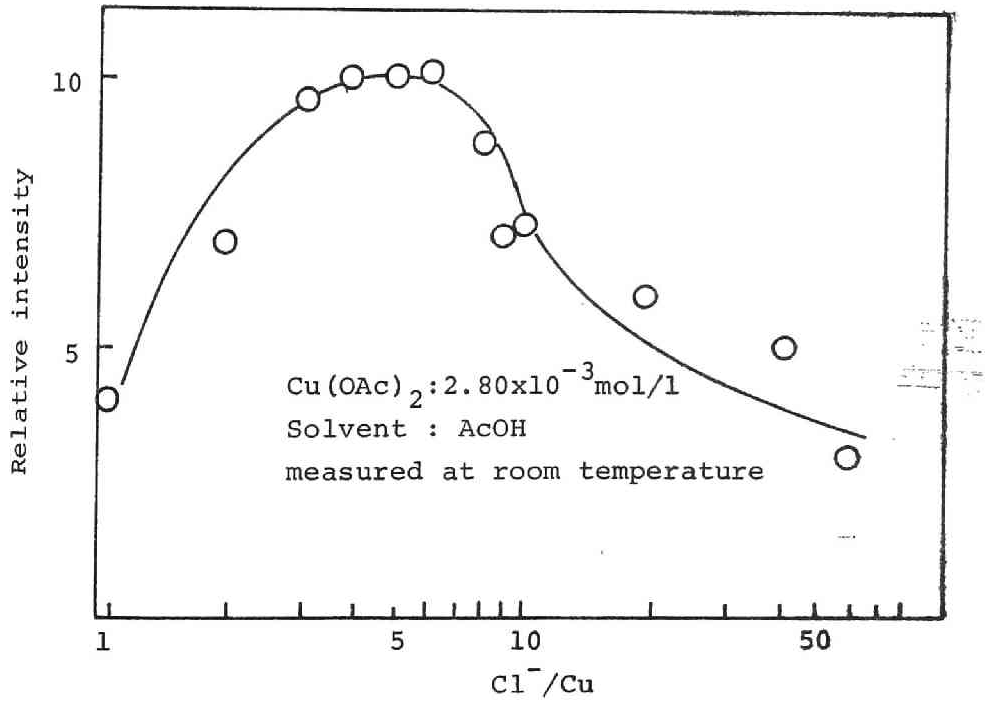


Fig. 10 Intensity of the ESR signal of Cu(II)-Cl relative to the intensity of Mn^{+2} marker

copper(II) acetate dimer (catalytically inactive) and, by coordinating to copper, forms monomer species (active) ..... It can be seen that excess lithium chloride rather decreases the intensity of the signal. Though the phenomenon cannot be explained well, it still has the same tendency as the results obtained in the oxidation of tetralin or the decomposition of THPO.

The temperature dependence of the ESR spectra of the catalyst system, Cu : Cl = 1 : 5, was observed and the result is shown in Fig. 11. We see that the spectrum observed at room temperature shows an asymmetric form with

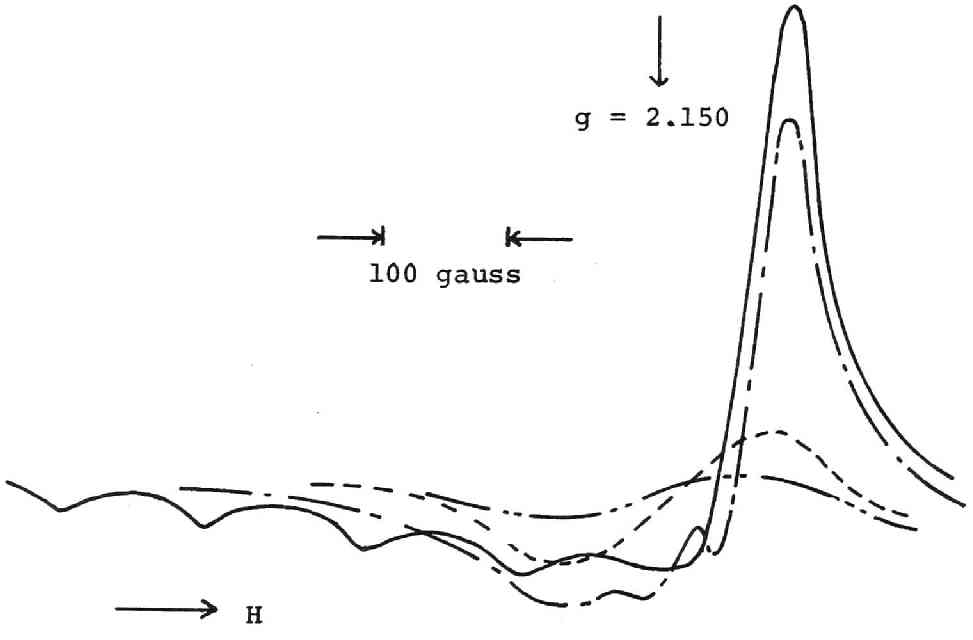


Fig. 11 Temperature dependence of the ESR spectra of Cu(II)-Cl system

$Cu(OAc)_2$: 2.80×10^{-3} mol/l
LiCl : 1.40×10^{-2} mol/l
Solvent : AcOH

—·— room temperature
——— $-40^{\circ}C$
– – – – $60^{\circ}C$
—··— $100^{\circ}C$

two small peaks near the center. It seems that these small peaks do not result from the interaction between the unpaired electron of copper with chloride ions which coordinated to copper, because the coupling constant of 71 gauss seems too large and, on cooling to $-40^{\circ}C$, they disappear. (see the figure) Moreover, the nuclear spin of chloride ion is 3/2 and there must be at least four peaks equally spacing. By the reasons mentioned above and the fact that the signal has an asymmetric form at room temperature where the free rotation of a molecule around its three axises is possible, it seems plausible that the signal consists of the mixture of several species. As can be seen from the figure, an anisotropic spectrum is obtained at $-40^{\circ}C$ in which the peak at highest magnetic field corresponds the resonance at $g_{\perp}$ (2.085) and the four peaks equally spacing corresponds the resonance at $g_{/\!/}$ (2.368). The value of $\bar{g}$ is obtained as 2.179 and the coupling constant ($A_{/\!/}$) is 119 gauss. It can be seen that the value of ($g_{/\!/} - 2$) is about four times that of ($g_{\perp} - 2$), which shows that the catalyst has a square planar configuration at low temperature. At higher temperatures ($60^{\circ}C$ or $100^{\circ}C$), the spectrum shows one broad singlet with a g-value of 2.150 which differs from the averaged one at $-40^{\circ}C$ (2.179). From these g-values and the spectrum obtained at room temperature, it seems that the catalyst system takes various composition at each temperature because the value of the equiliblium constants ($K_1 \sim K_4$) would vary with temperature.

$$Cu^{+2} \underset{Cl^-}{\overset{K_1}{\rightleftharpoons}} CuCl^{+} \underset{Cl^-}{\overset{K_2}{\rightleftharpoons}} CuCl_2 \underset{Cl^-}{\overset{K_3}{\rightleftharpoons}} CuCl_3^{-} \underset{Cl^-}{\overset{K_4}{\rightleftharpoons}} CuCl_4^{-2} \qquad (11)$$

As these values are not known now, we cannot estimate the species and the configuration of the most active catalyst system at the reaction temperature ($80^{\circ}C$).

The colour of the catalyst system, Cu ; Cl = 1 : 5, was yellow at room temperature but was found to turn to blue on cooling. Chughtai[21] reported that the visible spectra of $Cu(NCO)_4^{2-}$ and $CuCl_4^{2-}$ showed blue shift on cooling, which resulted from the change of these configurations from tetrahedral (at high temperature) to square planar (at low temperature). Taking this fact into consideration and judging from the spectrum at $-40^{\circ}C$, it can be considered that the most active catalyst system, Cu : Cl = 1 : 5, takes some configuration other than square planar one under the reaction condition.

Summary

The oxidation of 1,2,3,4-tetrahydronaphthalene catalyzed by copper(II) acetate was highly accelerated by addition of lithium chloride. The accelerating effect was found to be due to chloride ion which formed complex with copper. The mechanism of the oxidation by the catalyst system was discussed and the main initiating process was considered to be the catalytic decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide which was the intermediate product of the oxidation. This mechanism could explain the experimental result fairly well.

From the observation of the ESR spectra of the catalyst system, it was found that one of the accelerating effect of chloride ion was to decompose the catalytically inactive copper(II) acetate dimer and form active monomer species by coordinating to copper.

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Chapter 7 ESR Spectra of Alkoxy and Alkylperoxy Radicals

Introduction

The autoxidation of many hydrocarbons in the liquid phase is consistent with the following simplified mechanism:

$RH \xrightarrow{\cdots\cdot\cdots} R\cdot$		initiation
$R\cdot + O_2 \longrightarrow RO_2\cdot$		propagation
$RO_2\cdot + RH \longrightarrow ROOH$		
$ROOH \longrightarrow RO\cdot$ or $ROO\cdot$		degenerate branching
$2ROO\cdot\ (RO\cdot) \longrightarrow$ inactive product		termination

in which hydroperoxide (HPO) is formed as a first intermediate product followed by the decomposition to alkoxy or alkylperoxy radical which acts as a chain carrier.

As these radicals are generally short-lived, there have been not so many reports[1~3] concerning the ESR spectra of them except in the case of peroxy radicals obtained in the oxidation of polymer, where they are stabilized in polymer matrixes.[4~6] J.R.Thomas discussed the ESR spectrum of cumylperoxy radical in the oxidation of cumene by flow method and determined the steady state concentration of the radical.[7] Similarly, C.W.Chien et al. investigated the behaviour of t-butyl, cumyl, polypropylene and squalane peroxy radicals at low temperature by the use of ESR technique.[8] In all cases, it was reported that the spectra of peroxy radicals consisted of only one broad singlet and, therefore, structual information could not be obtained but that they could be distinguished from other alkyl radicals ($g \fallingdotseq 2.003$) by their considerably large g-values (2.014~2.019).[9]

As for alkoxy radicals, J.A.McMillan et al. dis-

cussed the ESR spectra of hydroxyl radical with a g-value of 2.009.[10] P.J.Sulliban et al. observed a spectrum obtained by U.V. irradiation on ethyl alcohol and assigned it (g = 2.014) as ethoxy radical[11] but, later, Ingold pointed out that the spectrum was of ethylperoxy radical.[12] Therefore, the distinction between the spectra of peroxy radicals and that of alkoxy radicals has not been clarified.

In this chapter, we have observed the ESR spectra of various alkylperoxy radicals obtained by U.V. irradiation on hydroperoxides and the results were compared with that of alkoxy radicals obtained by U.V. irradiation on alkyl nitrite. Hydrogen abstraction by these alkoxy and alkylperoxy radicals from solvent molecules was also studied at low temperature.

Experimental

Material Commercial t-butyl HPO, α,α'-dimethylbenzyl HPO (cumyl HPO) and t-butyl peroxide were distilled twice under reduced pressure and purified over activated alumina under a nitrogen atmosphere. Commercial α,α'-dimethylbenzyl peroxide (cumyl peroxide) was recrystallyzed twice from petroleum ether. 1,2,3,4-Tetrahydro-1-naphthyl HPO (tetralyl HPO) and benzyl HPO were synthesized by the same methods described in Chapter 1 and Chapter 3 respectively. Alkyl nitrites were obtained from the corresponding alcohol and sodium nitrite and distilled twice except in the case of ethyl nitrite. Boiling points of nitrites are shown below: allyl nitrite; 43.5 ~ 44.5°C, n-propyl nitrite; 50.2 ~ 51.0°C, iso-propyl nitrite; 38.0 ~ 38.5, n-butyl nitrite; 72.0 ~ 72.5°C, sec-butyl nitrite; 68.0 ~ 68.5°C, iso-butyl nitrite; 66.2 ~ 67.0°C, t-butyl nitrite; 57.0 ~ 58.5°C, n-amyl nitrite; 103.0 ~ 103.8°C, iso-amyl nitrite; 97.0 ~ 97.5°C, sec-amyl nitrite; 93.0 ~ 94.5°C, benzyl nitrite; 59.5 ~

60.5°C/12 mmHg, α,α'-dimethylbenzyl nitrite (cumyl nitrite); 78.0 ∼ 79.5°C/2mmHg.

Apparatus and procedures The apparatus used in the ESR experiment was the JES-3BS-X type of Japan Electron Optics Laboratory. For U.V. irradiation, the mercury lamp SHL-100 of Toshiba Co. Ltd. (the wave length of maximum intensity ; 560 nm) was used. Hydroperoxide or alkyl nitrite in a ESR sample tube made of quartz was degassed by a series of freeze-pump-thaw cycle and sealed. The temperature was maintained either by standing the sample tube in liquid nitrogen in a quartz dewar vessel or by passing cooled nitrogen gas through the low-temperature cavity. The cavity temperature was monitored with a thermocouple. Then the sample tube was placed in the center of the cavity and U.V. light was irradiated. Apectra were measured at the temperature range from -30°C to -196°C. Determination of g-value was made with Mn^{+2} marker as a standard.

Result and Discussion

Spectra obtained by the U.V. irradiation on hydroperoxides Benzyl, tetralyl, cumyl and t-butyl HPO were photolyzed at low temperature and the resultant radicals were observed by ESR spectrophotometer. As shown in Fig. 1, the spectrum obtained from benzyl HPO has an asymmetric form with no hyperfine structure at low temperature; that is, anisotropic g-factors are observed ($g_{\perp} = 2.003$, $g_{//} = 2.031$) at -196°C. However, at higher temperature (-140°C), the anisotropy becomes obscure and, at -108°C, the spectrum shows a broad symmetric singlet. At -70°C, no signal could be seen, which showed that the radical was unstable at this temperature and that the steady state concentration of the radical was very small. In Fig. 2, the result for tetralyl HPO is shown. We see that, in this case

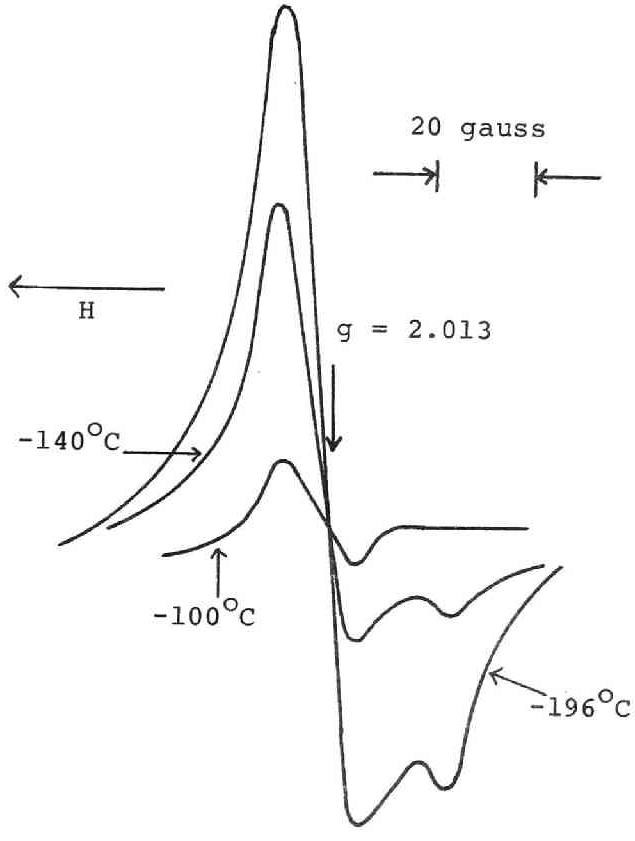

Fig. 1 ESR spectra obtained by the UV irradiation on benzyl HPO

also, a broad asymmetric signal is obtained with anisotropic g-factors in the temperature range from -100°C ~ -196°C ($g_{\perp}$ = 2.002, $g_{//}$ = 2.030). At -90°C, the spectrum becomes a symmetric singlet with a g-value of 2.010. It was found that similar spectra were also obtained by the U.V. irradiation on cumyl HPO or t-butyl HPO. From Table 1, we see that, in the case of cumyl HPO, three anisotropic g-factors are observed at low temperature (-160°C~ -196°C) but that, at higher temperature (-100°C), the signal shows a broad singlet with a g-value of 2.015. In the case of t-butyl HPO,

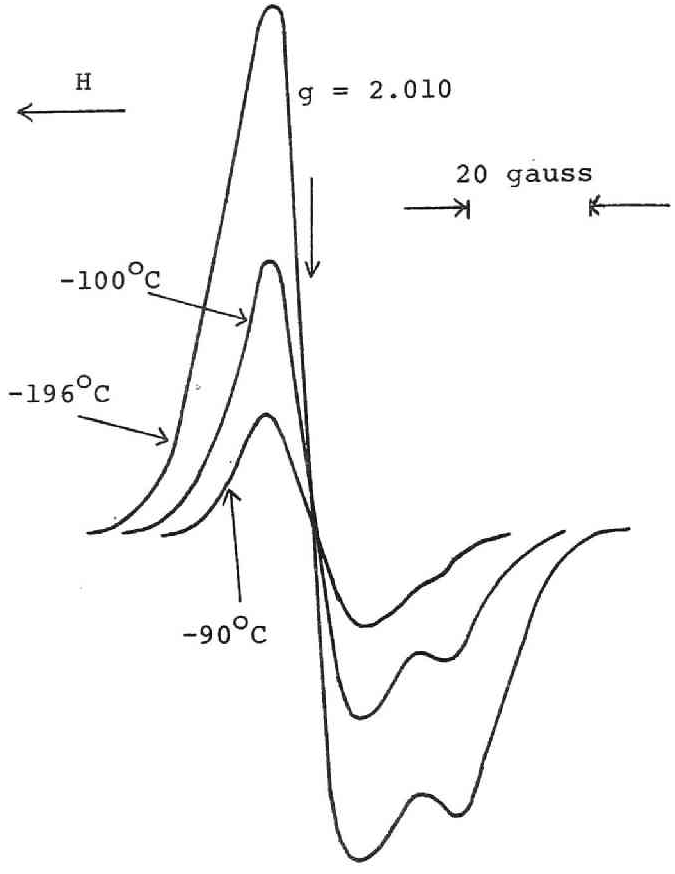

Fig. 2 ESR spectra obtained by the U.V. irradiation on tetralyl HPO

the spectrum shows an anisotropy at -90°C ~ -196°C, but, at -30°C, symmetric signal with a g-value of 2.012 appears.

From these results, it is seen that the spectra obtained by the U.V. irradiation on benzyl, tetralyl, cumyl, and t-butyl HPOs all show the same broad anisotropic forms at low temperature but that, at higher temperature, they become symmetric. It will also be noted that their g-values (2.010~ 2.017) are considerably larger than that of alkyl radicals (g ≒ 2.003).

In conclusion, the presented results suggest that these spectra are due to corresponding peroxy radicals which would be formed by the induced decomposition of HPO

Table 1 ESR spectra of peroxy radicals

Peroxy radical	Temp. (°C)	g-value
Benzyl peroxy radical	-196	$\bar{g}$=2.012 ($g_{\perp}$=2.003, $g_{//}$=2.031)
	-167	$\bar{g}$=2.013 ($g_{\perp}$=2.004, $g_{//}$=2.032)
	-140	$\bar{g}$=2.014 ($g_{\perp}$=2.005, $g_{//}$=2.032)
	-132	g=2.014
	-108	g=2.013
Tetralyl peroxy radical	-196	$\bar{g}$=2.012 ($g_{\perp}$=2.002, $g_{//}$=2.033)
	-100	$\bar{g}$=2.011 ($g_{\perp}$=2.003, $g_{//}$=2.030)
	-90	g=2.010
Cumyl peroxy radical	-196	$\bar{g}$=2.016 (g_{11}=2.003, g_{22}=2.014, g_{33}=2.033)
	-160	$\bar{g}$=2.017 (g_{11}=2.003, g_{22}=2.014, g_{33}=2.030)
	-127	$\bar{g}$=2.015 ($g_{\perp}$=2.004, $g_{//}$=2.021)
	-100	g=2.015
t-Butyl peroxy radical	-196	$\bar{g}$=2.013 ($g_{\perp}$=2.003, $g_{//}$=2.033)
	-90[a]	$\bar{g}$=2.012 ($g_{\perp}$=2.008, $g_{//}$=2.027)
	-30[a]	g=2.012
	-196[b]	$\bar{g}$=2.013 ($g_{\perp}$=2.004, $g_{//}$=2.032)

a) 10wt% in p-xylene b) t-Butyl HPO was decomposed by cobalt(II) stearate.

by alkoxy radical produced. (see below)* Alkoxy

$$ROOH \xrightarrow{U.V.} RO\cdot + \cdot OH$$

$$RO\cdot + ROOH \longrightarrow RO_2\cdot + ROH$$

radical is considered to be in low concentration to be detected.

It was found that the spectrum obtained by the decomposition of t-butyl HPO by cobalt(II) stearate was the same as that obtained by U.V. irradiation (last run in Table 1), which shows that t-butylperoxy radical is formed by the induced decomposition of the HPO by t-butoxy radical as shown below:**

$$t\text{-}BuOOH + Co(II) \longrightarrow t\text{-}BuO\cdot + OH^- + Co(III)$$

$$t\text{-}BuO\cdot + t\text{-}BuOOH \longrightarrow t\text{-}BuOH + t\text{-}BuOO\cdot$$

The g-value of cumylperoxy radical reported by Ingold[12] was 2.0145 ~ 2.0150 and that reported by Boss et al. was 2.0157 ~ 2.0177.[2] Boss et al. also reported that the g-value of t-butylperoxy radical was 2.012 ~ 2.0137.[2] These results are in good agreement with our's. In this work, we have carried out the U.V. irradiation on benzyl HPO (primary HPO) and tetralyl HPO (secondary HPO) in addition to tertiary HPOs and clarified that, generally, hydroperoxides (primary, secondary and tertiary) all produce corresponding peroxy radicals on U.V. irradiation and that ESR spectra of these radical show broad singlets with comparatively large

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*From the discussion given in the later section, the spectra proved not to be those of corresponding alkoxy radicals.

**To t-butyl HPO in a sample tube, p-xylene solution of cobalt(II) stearate was added with a syringe and the sample tube was cooled immediately with liquid nitrogen.

g-value (2.o10 ~ 2,017).

Spectra obtained by the U.V. irradiation on alkyl nitrites Sr. Patricia et al. discussed the spectra of methoxy and ethoxy radicals[13] and J. Q. Adams or J.K.Kochi et al. investigated the hydrogen abstraction from alcohols or hydrocarbons by t-butoxy radical.[14, 15] Spectrum of hydroxyl radical was also discussed.[16] However, there have not been so many reports and general informations concerning alkoxy radicals.

As alkyl nitrites (RONO) were reported to produce alkoxy radicals by photolysis, we have carried out the decomposition of alkyl nitrite by U.V. irradiation at low

$$RONO \xrightarrow{U.V.} RO\cdot + \cdot NO$$

temperature and observed the ESR spectra of the resultant radicals. Nitrites used were ethyl, allyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, t-butyl, n-amyl, sec-amyl, iso-amyl, benzyl, and cumyl nitrites. In Fig. 3, the spectrum obtained by the U.V. irradiation on cumyl nitrite at -196°C is shown. We see that the spectrum consists of a broad triplet spacing over about 100 gauss. Other spectra obtained, except in the case of t-butyl nitrite, were found to show the same triplet at -196°C, which suggests that the triplet obtained from cumyl nitrite

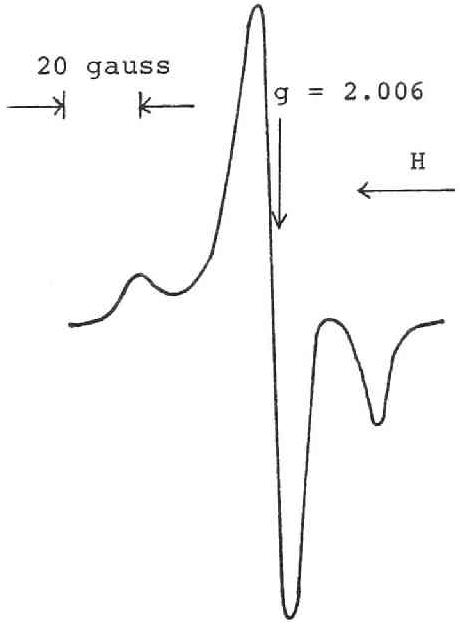


Fig. 3 ESR spectrum obtained by the U.V. irradiation on cumyl nitrite at -196°C

Table 2 Spectra obtained by UV irradiation on alkyl nitrite

Alkyl nitrite	g_{11}	g_{22}	g_{33}	$\bar{g}$
Ethyl nitrite	2.000	2.008	2.016	2.008
Allyl nitrite	2.000	2.008	2.017	2.008
n-Propyl nitrite	2.000	2.009	2.019	2.009
iso-Propyl nitrite	2.000	2.008	2.017	2.008
n-Butyl nitrite	2.000	2.007	2.015	2.007
sec-Butyl nitrite	2.002	2.009	2.015	2.008
iso-Butyl nitrite	2.000	2.008	2.016	2.008
n-Amyl nitrite	2.000	2.009	2.017	2.009
sec-Amyl nitrite	2.000	2.008	2.017	2.008
iso-Amyl nitrite	2.000	2.008	2.018	2.009
Benzyl nitrite	2.000	2.008	2.018	2.009
Cumyl nitrite	1.986	2.006	2.024	2.005

Spectra were measured at -196°C

or other nitrites cannot be attributable to the hyperfine structure but to the anisotropy of g-factors. In Table 2, g-values of these spectra at -196°C are shown. As can be seen from the table, three anisotropic g-factors are obtained in all cases; for example, g_{11} is 2.000, g_{22} is 2.007 and g_{33} is 2.015 in the case of n-butyl nitrites. Here we compare the spectra in Table 2 with those of peroxy radicals obtained previously. It can be seen that there is a definite difference between these g-values; for example, the spectrum obtained by the U.V. irradiation on cumyl nitrite has g_{11} factor of 1.986, g_{22} of 2.006, g_{33} of 2.003 and $\bar{g}$ of 2.005, while, in the case of cumyl peroxy radical, g_{11}=2.003, g_{22}=2.014, g_{33}=2.033 and $\bar{g}$ = 2.016. Moreover, there could be found no similarity between the forms of these two spectra. Also, no similarity can be seen between the spectrum of benzylperoxy radical and that obtained by the U.V. irradiation on benzyl nitrite. (compare Fig. 1 and Fig. 2) It can be seen from Table 2 that, in all cases, similar spectra with $\bar{g}$ value of $2.005 \sim 2.009$ are obtained by the irradiation on nitrites and that these g-values are smaller than those of peroxy radicals ($2.010 \sim 2.017$) but larger than those of alkyl radicals ($g \fallingdotseq 2.003$). Therefore, it seems plausible that alkoxy radicals are formed by the U.V. irradiation on alkyl nitrites. Sullivan et al. obtained the spectra of methoxy and ethoxy radicals by the U.V. irradiation on methyl and ethyl alcohol at -196°C and reported that these spectra had two anisotropic g-factors.[11] However, in our case, the spectrum of ethoxy radical has three anisotropic g-factors at -196°C. As can be seen from Table 2, all the spectra of alkoxy radicals, except in the case of cumyloxy radical, have similar g-values; that is, there is little difference in g-value due to the difference of the configuration of alkoxy radicals. For example, g-value of the spectrum of conjugated allyl-

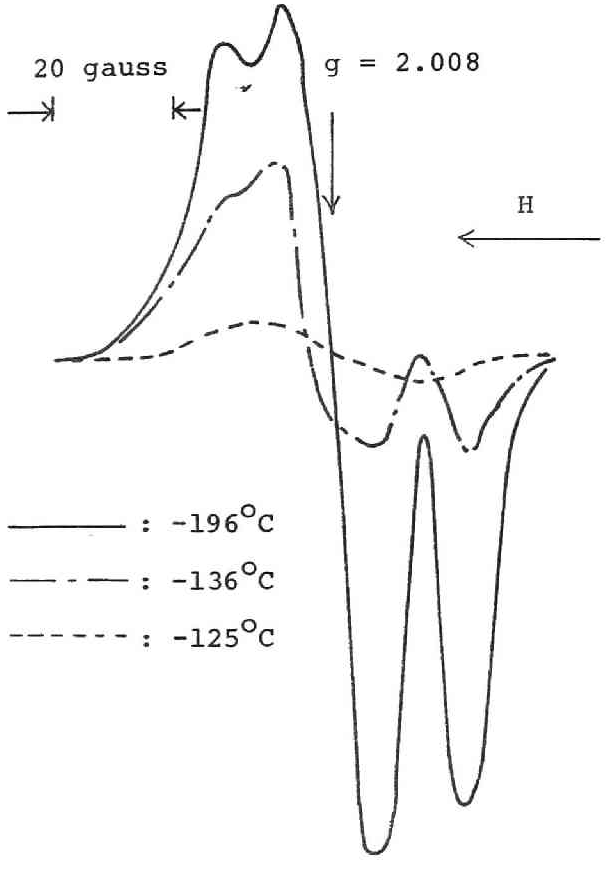


Fig. 4 Spectra obtained by the U.V. irradiation on benzyl nitrite

oxy radical is almost the same as that of other non-conjugated alkoxy radicals. However, in the case of peroxy radicals, g-values were found to vary considerably. (see Table 1) The difference between alkoxy radicals and peroxy radicals seems to result from the fact that the unpaired electron of peroxy radical interacts with the substitute on α-carbon atom through the conjugated system of two oxygen atoms, while the unpaired electron of alkoxy radical is restricted on the oxygen atom. Fig. 4 shows the temperature dependence of the spectrum of benzyloxy radical. We see that three anisotropic g-factors are observed at -196°C but, at -136°C, only

two g-factors ($g_{\perp}$ = 2.003, $g_{//}$ = 2.017 and $\bar{g}$ = 2.008) are obtained. At -125°C, a broad singlet with a g-value of 2.008 is observed and, above -120°C, no signal could be seen. Also, in the case of other alkoxy radicals, no signal could be seen above -160°C, which shows that the rate of the decay of alkoxy radical is larger than that of peroxy radicals.

Spectra obtained by the U.V. irradiation on t-butyl nitrite or t-butyl peroxide t-Butyl nitrite was photolyzed at -196°C and the resultant spectrum is shown in Fig. 5. We see that, different from other nitrites, a spectrum due to t-butoxy radical cnnot be observed but, instead, a complex spectrum appears.

Spectrum obtained by the U.V. irradiation on t-butyl peroxide is also shown in Fig. 5. Though, in some literatures, it was described that no spectrum could be obtained by the photolysis of t-butyl peroxide, we see that a similar complex signal as in the case of t-butyl nitrite is obtained. These two resemble to one another and contains quartet which is analyzed as the signal of methyl radical in terms of coupling constant of 23 gauss and g-value of 2.003. From the results shown in Fig. 5, it seems that t-butoxy radical undergoes fragmentation at this temperature to give methyl radical*** Other signal could not be determined.

Hydrogen abstraction by cumyloxy and cumylperoxy radicals from cumene It is important to discuss the hydrogen abstraction by alkoxy or alkylperoxy radical which constitutes the radical chain in the autoxidation of hydrocarbons. Therefore, we have studied the interaction of cumylperoxy radical or cumyloxy radical with cumene by the use of ESR technique.

***T.Shida reported that methyl radical was produced by the γ-ray irradiation on di-t-butyl peroxide.[18)]

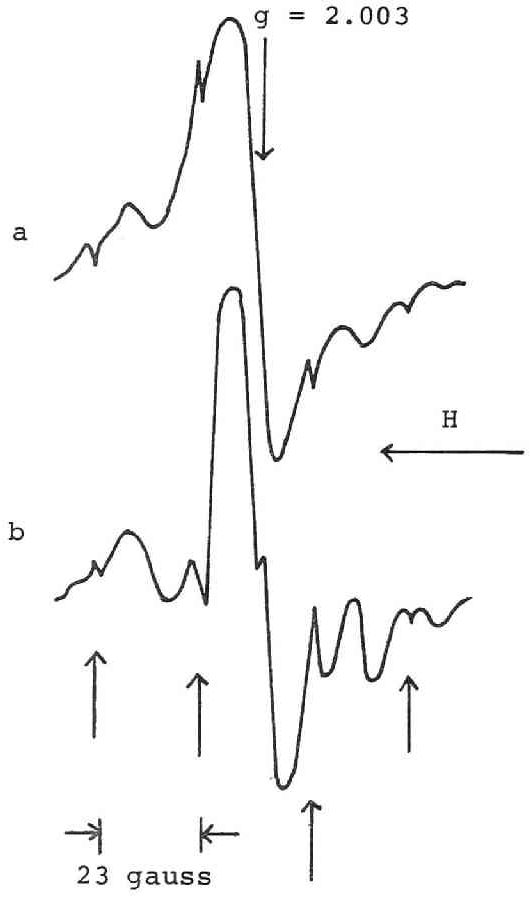


Fig 5 ESR spectra obtained by the U.V. irradiation on t-butyl peroxide and t-butyl nitrite at -196°C

a : t-Butyl peroxide

b : t-Butyl nitrite

↑ : Spectrum of methyl radical

When cumyl nitrite in cumene (30wt%) was irradiated for about 30 minutes, a signal with a obscure hyperfine structure (g=2.003) was obtained instead of the spectrum of cumyloxy radical. (see Fig. 6) It seems unlikely that the radical was formed by the U.V. irradiation of solvent cumene because no signal could be observed by the

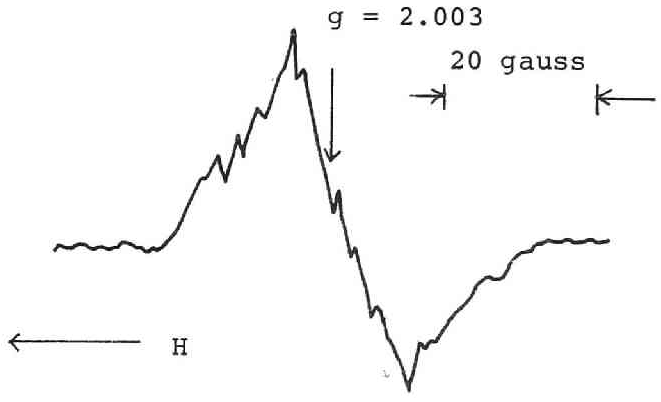


Fig. 6 ESR spectra obtained by the U.V. irradiation on cumyl nitrite in cumene at -196°C [Cumyl nitrite] : 30 wt%

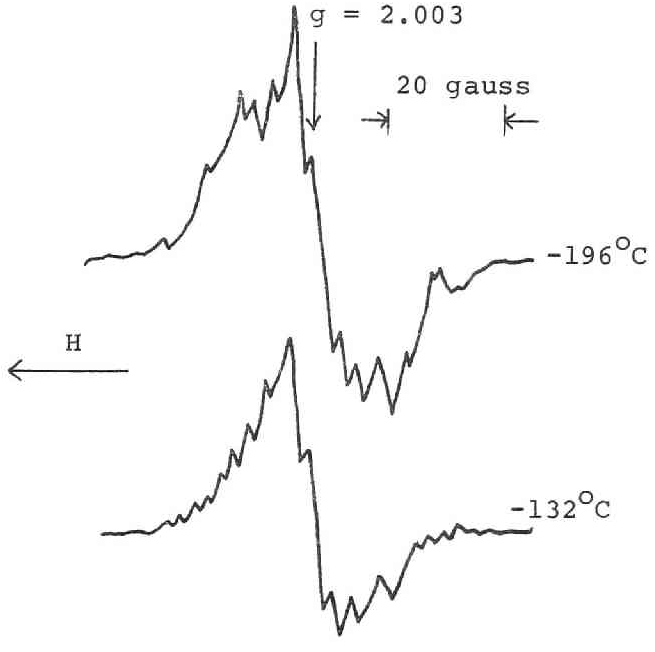
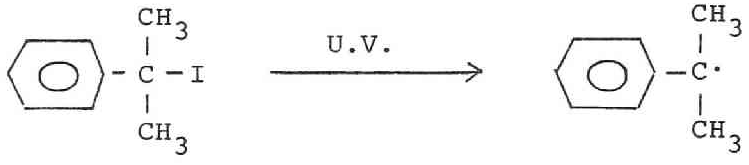


Fig. 7 ESR spectra obtained by the U.V. irradiation on cumyl iodide

phtolysis of pure cumene for only 30 minutes. As can be seen from Fig. 7, when cumyl iodide was irradiated, the spectrum similar to that in Fig. 6 was observed with a g-value of 2.003 at $-132 \sim -196^{\circ}C$. It seems that, in the case of cumyl iodide, cumyl radical is formed by the U.V. irradiation.



We have also carried out the photolysis of pure cumene for several hours at $-196^{\circ}C$ and the result is given in Fig. 8. The spectrum so obtained resembled to that in the case of cumyl nitrite in cumene or cumyl iodide. Moreover, in this case, the signal of hydrogen atom formed by the homolysis of cumene was observed with

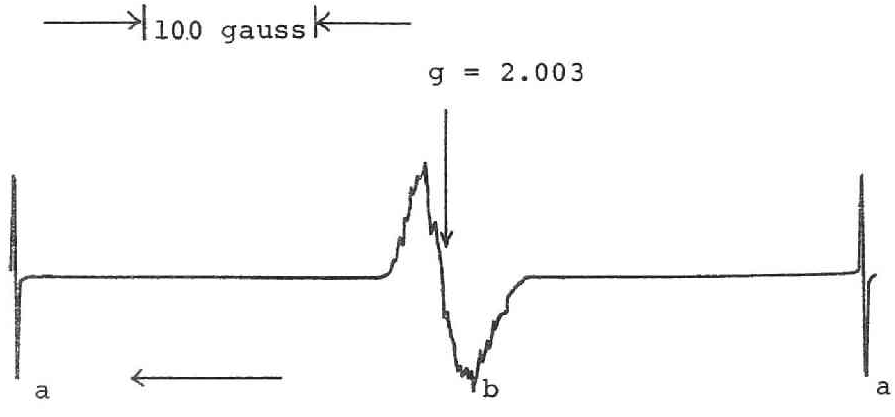


Fig. 8 ESR spectrum of cumyl radical obtained by the U.V. irradiation on cumene at $-196^{\circ}C$

a : Hydrogen radical

b : cumyl radical

a hyperfine coupling constant of 508 gauss. Compared the result in Fig. 6 with that in Fig. 8 and Fig. 9, we concluded that the spectrum obtained by the photolysis

of cumyl nitrite in cumene was that of cumyl radical, which was formed by the hydrogen abstraction from cumene by cumyloxy radical.

$$RONO \xrightarrow{U.V.} RO\cdot + \cdot NO$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

RH : cumene

It can be seen from Fig. 9 that the spectrum obtained by the photolysis of cumyl peroxide in cumene (30 wt%) also resembles to those shown in Fig. 6 ~ Fig. 8. It seems that, in this case also, cumyl radical is produced

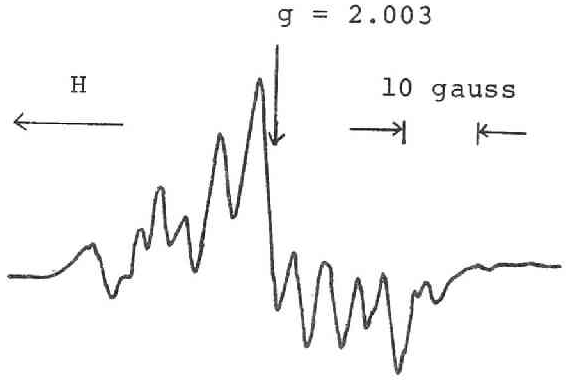


Fig. 9 ESR spectrum obtained by the U.V. irradiation on cumyl peroxide in cumene at -132°C

[Cumyl peroxide] : 30 wt%

by the hydrogen abstraction from cumene.

$$ROOR \xrightarrow{U.V.} 2RO\cdot$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

RH : cumene

When cumyl HPO in cumene (30 wt%) was photolyzed at -90°C ~ -196°C, only the spectrum of cumylperoxy radical could be observed, which shows that, at this low temperature, hydrogen abstraction by cumylperoxy radical does not proceed. From the result obtained, it can be concluded

that the ability of cumyloxy radical to abstract hydrogen is larger than that of cumylperoxy radical. However, as it is generally considered that peroxy radicals abstract hydrogen more easily than alkoxy radicals, further experiments as for other alkoxy and alkylperoxy radicals are necessary.

Summary

ESR spectra of four hydroperoxides (benzyl, tetralyl, cumyl and tert-butyl hydroperoxides) and thirteen alkyl nitrites (ethyl, allyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-amyl, iso-amyl, sec-amyl, benzyl and cumyl nitrites) have been observed under U.V. irradiation at temperature range from $-30^{\circ}C \sim -196^{\circ}C$. It was found that the corresponding peroxy radicals and alkoxy radicals were produced from the hydroperoxides and the nitrites respectively. On the basis of the difference between the g-values, it may be said that the spectra of alkoxy radicals ($g = 2.005 \sim 2.009$) are clearly distinguished from that of peroxy radicals ($g = 2.010 \sim 2.017$).

ESR spectra of cumene solution of cumyl nitrite, cumyl peroxide and cumyl hydroperoxide under U.V. irradiation at the temperature below $-132^{\circ}C$ were also observed. From the result obtained, it was found that the ability of hydrogen abstraction by cumyloxy radical from cumene was larger than that by cumylperoxy radical.

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Appendix

ESR Study for Hydrogen Abstraction by Alkoxy Radicals

Introduction

An abstraction of hydrogen atom by alkoxy radical is an important step in the liquid-phase oxidation of hydrocarbon. By the use of ESR technique with flow method, J.Q.Adams discussed the abstraction of hydrogen by t-butoxy radical from various alcohols and reported that hydrogen atom of the α-position was mainly abstracted.[1] In the same method, J.K.Kochi et al. studied this process in various hydrocarbon solvents at low temperature.[2] However, in their experiment, alkoxy radical used was only t-butoxy radical and investigations with n- or sec-alkoxy radicals have scarcely been carried out.

In this work, we have studied the abstraction of hydrogen atom by n-, sec-, iso- and t-butoxy radicals and cumyloxy radical from alcohols, ether or hydrocarbon solvent.

Experimental

Preparation of the reagents and the procedures for the observation of ESR spectra were the same as described previously.

Result and Discussion

Di-t-butyl peroxide, dicumyl peroxide, cumyl nitrite and n-, sec-, iso- and t-butyl nitrites were photolyzed at $-136^{\circ}C \sim -196^{\circ}C$ in various solvents and the resultant radicals were observed. Fig. 1 shows the ESR spectra obtained by U.V. irradiation on methyl alcohol, t-butyl peroxide in methyl alcohol (30wt%) and t-butyl nitrite in methyl alcohol (30wt%). These three spectra all

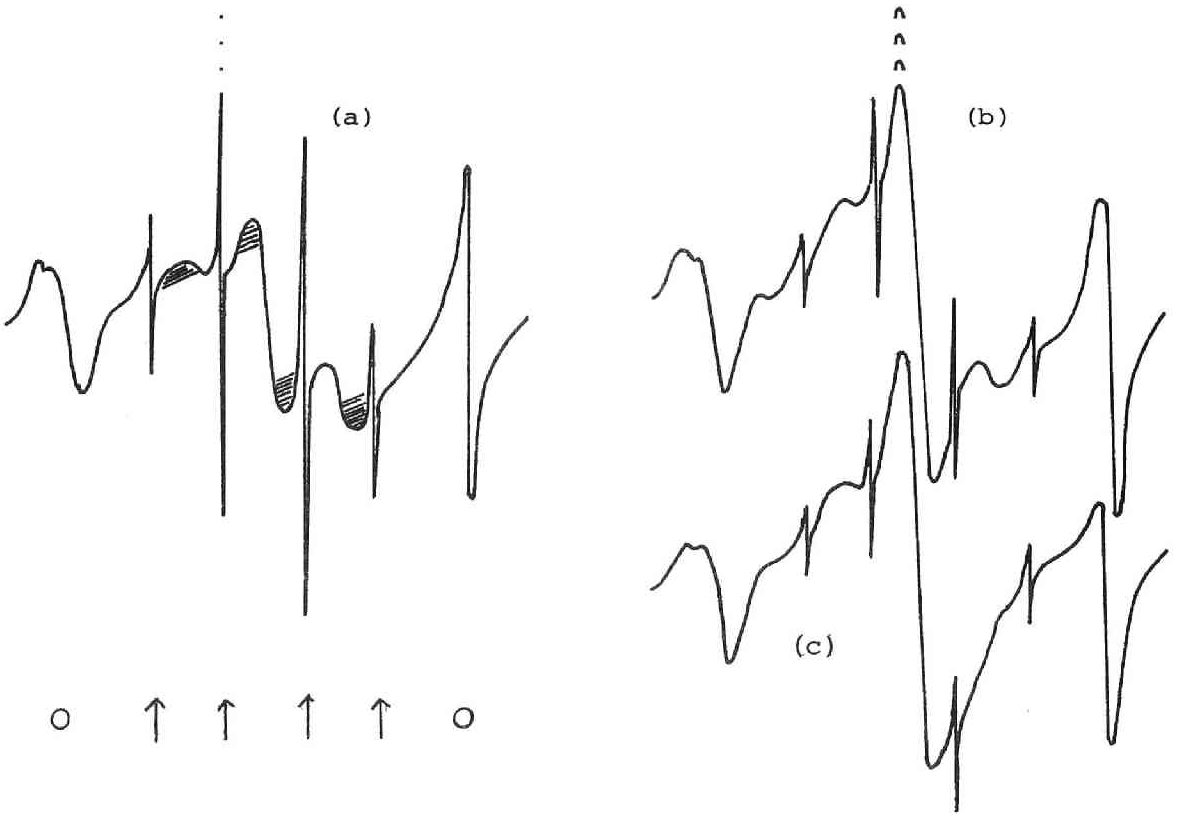

Fig. 1 ESR spectra obtained by the U.V. irradiation on (a) methyl alcohol (b) di-t-butyl peroxide in methyl alcohol (30 wt%) (c) t-butyl nitrite in methyl alcohol (30 wt%) at -196°C for 20 minutes

↑ methyl radical, O formyl radical, ▨ methanol radical

contain signals of formyl radical ($\dot{C}HO$, hyperfine coupling constant (A) = 138 gauss), methyl radical ($\dot{C}H_3$, A = 23 gauss) and a broad triplet of methanol radical ($\dot{C}H_2OH$, A = 17 gauss). We see that, in the case of t-butyl peroxide or t-butyl nitrite, an unknown broad spectrum is superimposed upon the signals mentioned above, which could not be identified.* However, in both cases, the signal due to t-butoxy radical could not be obtained.

The results for other nitrites are shown in Table 1. We see that, in the case of n-, sec-, or iso-butyl nitrites in methyl alcohol, corresponding alkoxy radicals are observed in addition to the radicals formed from methyl alcohol, which shows that these alkoxy radicals are trapped in the solvent matrix.

It is seen that ethyl radical and ethanol radical ($CH_3\dot{C}HOH$) can be observed by the U.V. irradiation of t-butyl peroxide or t-butyl nitrite in ethyl alcohol and, in the case of n-, sec-, and iso-butyl nitrite in ethyl alcohol, corresponding alkoxy radicals were also obtained in addition to these radicals.

In iso-propyl ether or cumene solvent, U.V. irradiation on n-, sec- or t-butyl nitrites produces only corresponding alkoxy radicals. However, in the case of t-butyl nitrite or t-butyl peroxide, it is seen that iso-propyl ether radical (heptet with a hyperfine coupling constant of 22 gauss) or cumyl radical is observed.

From these results, it can be deduced that the reactivity of t-butoxy radical is larger than that of n-, sec-, or iso-butoxy radical. As described previously, t-butoxy radical was found to undergo

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*This signal was also observed by the U.V. irradiation on pure t-butyl peroxide or t-butyl nitrite. (see the previous section in this chapter)

Table 1 ESR spectra obtained by the U.V. irradiation on t-butyl peroxide and alkyl nitrites at low temperature

Solvent	Methyl alcohol	Ethyl alcohol	iso-Propyl ether	Cumene
Temperature	-196°C	-196°C	-196°C	-136 -196°C
Peroxide or Nitrites	Radicals observed			
n-Butyl nitrite	RO·, ·CH_3, ·CHO ·CH_2OH	RO·, ·C_2H_5 $CH_3\dot{C}HOH$	RO·	RO·
sec-Butyl nitrite	RO·, ·CH_3, ·CHO ·CH_2OH	RO·, ·C_2H_5 $CH_3\dot{C}HOH$	RO·	RO·
iso-Butyl nitrite	RO·, ·CH_3, ·CHO ·CH_2OH	RO·, ·C_2H_5 $CH_3\dot{C}HOH$	RO·	RO·
t-Butyl nitrite	·CH_3, ·CHO, ·CH_2OH	·C_2H_5, $CH_3\dot{C}HOH$	$(CH_3)_2\dot{C}OCH(CH_3)_2$	$C_6H_5\dot{C}(CH_3)_2$
t-Butyl peroxide	·CH_3, ·CHO, ·CH_2OH	·C_2H_5, $CH_3\dot{C}HOH$	$(CH_3)_2\dot{C}OCH(CH_3)_2$	$C_6H_5\dot{C}(CH_3)_2$
Cumyl nitrite			RO·	$C_6H_5\dot{C}(CH_3)_2$

The U.V. irradiation was carried out for about 20 minutes except in the case of cumyl peroxide(30 minutes). RO· shows a corresponding alkoxy radical

fragmentation to produce methyl radical**, while n-, sec-, or iso-butoxy radical did not. From this, it seems that t-butoxy radical owes its high activity to methyl radical formed by the fragmentation as shown below:

$$\text{t-BuOOBu-t} \xrightarrow{\text{U.V}} \text{t-BuO}\cdot \longrightarrow \text{CH}_3\cdot$$
$$\text{t-BuONO}$$

$$\text{CH}_3\cdot + \text{SH} \longrightarrow \text{CH}_4 + \text{S}\cdot$$

SH : solvent

In methyl alcohol or ethyl alcohol, t-butoxy radical (or methyl radical formed by the fragmentation) might also abstract hydrogen from solvents. However, as solvent radicals were also formed by the U.V. irradiation on pure alcohols, it could not be confirmed.

Though cumyloxy radical, different from t-butoxy radical, was found not to undergo fragmentation to produce active methyl radical at this low temperature, it can still abstract hydrogen atom from cumene.

From the results obtained so far, it may be concluded that the activity of tertiary alkoxy radicals in the abstraction of hydrogen is higher than that of primary, secondary or iso-alkoxy radical.

** Sweiner et al. reported that t-butoxy radical could not be obtained by the U.V. irradiation on t-butyl peroxide.[3)]

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General Conclusion

In the studies presented in this thesis, the author has intended to elucidate the catalytic action of copper salts in the liquid-phase oxidation of hydrocarbons or in the decomposition of hydroperoxides. Also some discussions concerning the nature of the intermediate radicals in the oxidation and the interaction of copper salts with these radicals were carried out. Chapters 1 ~ 3 deal with the decomposition of primary, secondary and tertiary hydroperoxides catalyzed by copper chlorides in basic solvents. Chapter 4 deals with the discussion for the interaction of copper salt with primary and secondary hydroperoxides by the use of MO calculation. Catalytic action of cobalt salt was also investigated and compared with that of copper salt. Chapter 5 ~ 6 describe the oxidation of hydrocarbons catalyzed by copper salt - alkali chloride system, in which the effect of chloride ion to the activity of copper salts was discussed. Chapter 7 deals with the ESR spectra of alkoxy and alkylperoxy radicals.

In Chapter 1, the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide catalyzed by copper chlorides was investigated in basic solvents. It was suggested that copper(I) chloride decomposed THPO by a radical reaction and the proposed mechanism agreed with the experimental results fairly well. Copper(II) chloride was considered to decompose THPO by an ionic dehydration proceeding through an abstraction of α-hydrogen of THPO by basic solvent. In both catalytic reactions, water and α-tetralone were obtained selectively, which suggested that basic solvents exerted the remarkable effect upon α-tetraloxy radical.

In Chapter 2, the decomposition of α,α'-dimethylbenzyl hydroperoxide (CHPO) catalyzed by copper chlorides in

pyridine was studied. Copper(I) and copper(II) chlorides both were found to decompose CHPO by a radical mechanism, but the activity of copper(I) chloride was much higher than that of copper(II) chloride. Induction period, which appeared in the case of copper(II) chloride, was diminished by the addition of reducing agents as the result of the reduction of copper(II) to copper(I), but prolonged by oxidizing agents which oxidized copper(I) to copper(II). From these results, it was deduced that the transformation from copper(II) to copper(I) occurred during the induction period. Though the evidence for the direct decomposition of CHPO by copper(II) could not be obtained, its possibility cannot yet be ruled out during the induction period.

Chapter 3 deals with the decomposition of benzyl hydroperoxide (BHPO) catalyzed by copper chlorides in pyridine. In a nitrogen atmosphere, it was found that copper(I) and copper(II) chlorides both decomposed BHPO by a radical reaction. However, in the presence of oxygen, where an active copper(I) species was oxidized to copper(II), copper(II) chloride decomposed BHPO by an ionic dehydration as in the case of THPO. The effect of some basic solvents for benzyloxy radical was also discussed and it was deduced that copper - basic solvent system, not copper salt or basic solvent alone, promoted the formation of benzaldehyde.

Chapter 4 deals with the MO calculation for an interaction of $Cu(NH_3)Cl_2$ with methyl and 1-methylallyl hydroperoxides. It was found that copper(II) attacked the O_1 of these hydroperoxides ($R\text{-}O_1\text{-}O_2\text{-}H$) and weakened the carbon-hydrogen bond of the α-position of the hydroperoxides, which could explain the catalytic action of copper(II) in the ionic dehydration of primary or secondary hydroperoxide in basic solvents. The interaction of $Co(OH)_5$ with methyl hydroperoxide was discussed and the

result was compared with that of $Cu(NH_3)Cl_2$. The possibility of copper(II) salt to promote the direct decomposition of hydroperoxides was also suggested.

In Chapter 5, the study for the oxidation of cyclohexene catalyzed by copper(II)-Cl system in glacial acetic acid was carried out. The catalytic activity of copper(II) chloride was highly accelerated by the addition of various alkali chlorides. The activation of copper salt was found to be due to the coordination of chloride ion to copper salt as a ligand. In the course of the reaction, the catalyst system lost its activity owing to the consumption of chloride ion; chloride ion was found to be transformed into trans-2-chlorocyclohexanol-(1) by the chlorination of the oxidation products, cyclohexenone or cyclohexenol.

In Chapter 6, the catalytic activity of copper(II) acetate - lithium chloride system in the oxidation of 1,2,3,4-tetrahydronaphthalene was discussed. Chloride ion was also found to accelerate the reaction. The mechanism of the oxidation was proposed in which the initiation was considered to proceed through the catalytic decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide. By the use of ESR technique, it was found that one of the accelerating effect of chloride ion was to decompose the catalytically inactive dimer structure of copper(II) acetate and form active monomer species by coordinating to copper.

Chapter 7 deals with the ESR spectra of alkoxy and alkylperoxy radicals at low temperature. By the U.V. irradiation on hydroperoxides(benzyl, tetralyl, cumyl and t-butyl hydroperoxides) the spectra of the corresponding peroxy radicals ($g = 2.010 \sim 2.017$) were obtained. By the decomposition of alkyl nitrites (ethyl, allyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, t-butyl, n-amyl, iso-amyl, sec-amyl, benzyl and cumyl nitrites),

the spectra of the corresponding alkoxy radicals(g=2.005 ~ 2.009) were obtained. On the basis of the difference between the g-values, alkoxy radicals could be clearly distinguished from peroxy radicals. Hydrogen abstraction by cumyloxy radical, n-, sec-, iso- and t-butoxy radicals from some solvents was also studied and it was shown that t-alkoxy radicals abstracted hydrogen more easily than n-, sec-, or iso-alkoxy radical.

From the results obtained in this thesis, it is considered that the catalytic behaviour of copper salt is different from other transition metals; for example, as described in Chapter 1, cobalt, nickel or manganese was found to be inactive in the decomposition of hydroperoxide in such a strong base as pyridine. Moreover, in the oxidation of hydrocarbons, the accelerating effect of chloride ion was observed only in the case of copper salt. (Chapter 5) These may be due to the ability of copper salt to undergo ligand exchange easily compared with other transition metals. This ability is shown by the chlorination of olefine by copper(II)-chloride ion system in the presence of hydroperoxide and can be utilized in the further synthetic procedure. In all the work, the activity of copper salt was found to be attributed to its ability to decompose hydroperoxide, but the possibility of copper(II) to initiate the direct decomposition of hydroperoxide was remained unclarified. No other effect, such as an activation of a molecular oxygen or a direct abstraction of hydrogen from hydrocarbon, could be seen.